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Chemically Active Fluid Bed for SOx Control
Volume I. Process Evaluation Studies

Westinghouse Research and Development Center
Pittsburgh, PA

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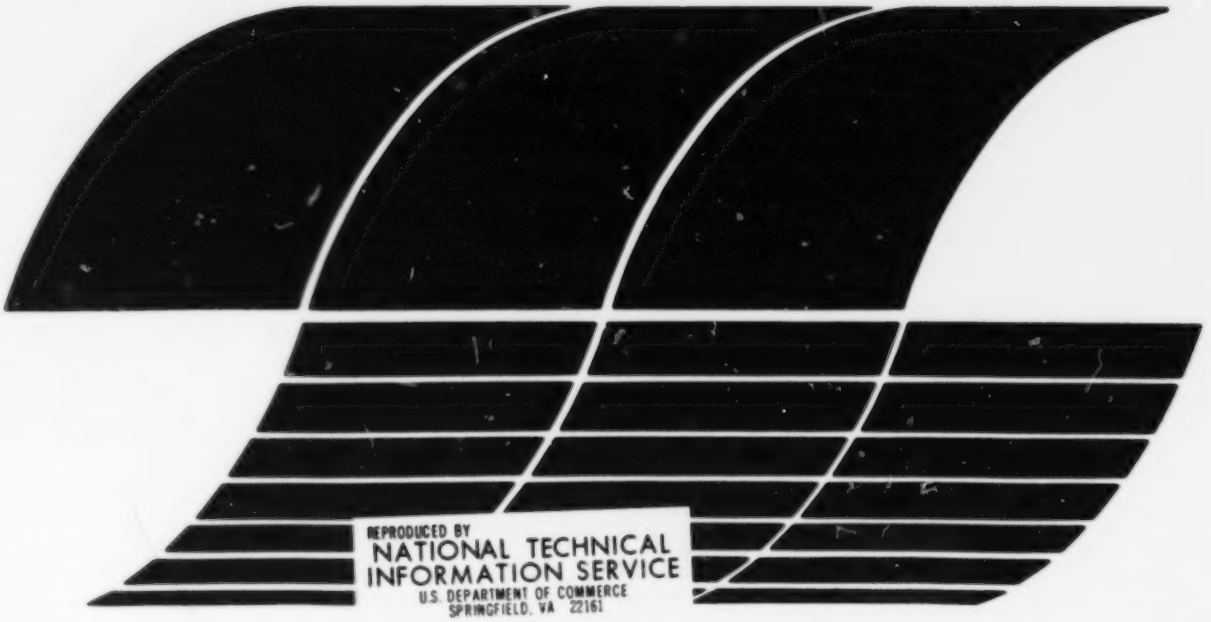

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16. ABSTRACT The report describes selected process evaluation studies supporting the development of an atmospheric-pressure, fluidized-bed, chemically active gasification process, using a regenerative limestone sulfur sorbent to produce low- to intermediate-Btu fuel gas. Limestone sorbent selection and attrition, alternative medtal oxide sorbents, particulate control, fuel supply, and an updated process assessment are investigated. Limestone sorbent selection results are presented for the EPA-sponsored CAFB demonstration plant. Sorbent attrition and economics are the main criteria as most limestone are not limited by sulfur removal. Trace element, regeneration, and disposal characteristics should be considered. Feasibility tests of air oxidation for disposal of gasifier solids for once-through operation show up to 70% conversion of the CaS. Methods for improving performance are identified. A procedure was developed to measure the attrition tendency of the sorbent selected. Brownwood limestone has intermediate attrition resistance showing 5.4% mass loss by attrition for this test, compared with three reference stones ranging from 0.5 to 9.1%. Sixteen alternative metal oxide sulfur sorbents that could reduce the environmental impact of solids disposal and may improve process economics were screened. CaO/CaO3, ZnO, and FeO are sorbents identified for further study.

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PREFACE

The Westinghouse Research and Development Center is carrying out a program under contract to the United States Environmental Protection Agency (EPA) to provide experimental and engineering support for the development of the Chemically Active Fluid-Bed (CAFB) process. The process was originally conceived at the Esso Research Centre, Abingdon, UK (ERCA), as a fluidized-bed gasification process to convert heavy fuel oils to a clean, medium heating-value fuel gas for firing in a conventional boiler. Westinghouse, under contract to EPA, completed an initial evaluation of the process in 1971.[1] Conceptual designs and cost estimates were prepared for new and retrofit utility boiler applications using heavy fuel oil. Westinghouse continued the process evaluation from 1971 to 1973 and formulated an atmospheric pollution control demonstration plant program for retrofit of a utility boiler utilizing a high-sulfur, high-metal-content fuel oil (for example, vacuum bottoms).[2] The CAFB process represented an attractive option for use of these low-grade fuels for which pollution control using hydrodesulfurization or stack-gas cleaning was uneconomical. Application of a pressurized CAFB concept with combined-cycle power plants was also assessed.[2] Experimental support work was initiated between 1971 and 1973 to investigate two areas of concern - sorbent selection and spent sorbent processing - to achieve an acceptable material for disposal or utilization. The preliminary design and cost estimate for a 50 MW_e demonstration plant at the New England Electric System (NEES) Manchester Street Station in Providence, RI were completed in 1975.[3] Commercial plant costs were projected and development requirements identified. Experimental support of the sulfur removal system continued in order to provide a basis for the detailed plant design. A number of design and operating parameters from the preliminary design study that required further development were identified. This three-volume report presents results of process

analyses, experimental studies, and application evaluations carried out from 1976 to June 1979. This volume contains an assessment of the market potential, sulfur control studies on limestone selection and attrition, alternative sulfur sorbents, particulate control, and process assessment. Our conclusions are based on available CAFB experimental data and on Westinghouse analyses of CAFB plant designs and performance projections. Results and analyses of exploratory tests with lignite in a CAFB pilot plant ($\sim$1 MW_e) currently being completed by Esso Research Centre and of the lignite tests scheduled at Central Power and Light Co.'s 10 MW plant are not included in this report. Our conclusions are subject to the results and analyses of these experimental programs.

Volumes II and III of this report and prior reports issued under this contract include:

- Chemically Active Fluid Bed for SO_x Control: Volume 2. Spent Sorbent Processing for Disposal/Utilization, EPA-600/7-79-158b, December 1979
- Chemically Active Fluid Bed for SO_x Control: Volume 3, Sorbent Disposal, EPA-600/7-79-158c, July 1979
- Solids Transport between Adjacent CAFB Fluidized Beds, EPA-600/7-79-021, January 1979
- Sorbent Selection for the CAFB Residual Oil Gasification Demonstration Plant, EPA-600/7-77-029, NTIS PB 266 827, March 1977.

ABSTRACT

Selected process evaluation studies are reported in support of the development of an atmospheric-pressure fluidized-bed gasification process referred to as the Chemically Active Fluid Bed (CAFB) process. The basic concept was designed for liquid fuels and utilizes a regenerative limestone sulfur sorbent and produces a low- to intermediate-Btu fuel gas. Limestone sorbent selection, sorbent attrition, alternative metal oxide sorbents, particulate control, residual fuel feedstock availability, and an updated process assessment are investigated. Limestone sorbent selection results are presented for the EPA-sponsored CAFB demonstration plant. Sorbent attrition and economics provide the primary criteria, as most limestones are not limited by sulfur removal. Trace element, regeneration, and disposal characteristics should be considered. An attrition tendency procedure was developed and utilized to measure the attrition tendency of the Brownwood limestone sorbent selected for the demonstration plant. Alternative metal oxide sulfur sorbents are reviewed that could reduce the environmental impact of solids disposal and may improve process economics. Three sorbents are identified for further study. Particulate control requirements are identified for coal and residual fuels. The availability of residual fuels for the process are reviewed, as are the environmental impact of the process and operational considerations. Application of the process will depend on the availability of suitable feedstocks. Process modification for solid fuel application could permit utilization of the process since availability of high-sulfur residual oils will be increasingly limited to refinery applications.

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NOMENCLATURE

CAFB - Chemically active fluidized bed

DOE - Department of Energy

EPA - Environmental Protection Agency

ERCA - Esso Research Centre, Abingdon, UK

FW - Foster Wheeler Corporation

MeO - Metal oxide

NEES - New England Electric System

PER - Pope, Evans and Robbins

TGA - Thermogravimetric analysis (analyzer)

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Numerous individuals at Westinghouse contributed. We gratefully acknowledge the thoughtful and perceptive reviews and contributions of Dr. D. H. Archer, Manager Chemical Engineering Research; and the work of A. W. Fellers, C. A. Hill, and R. E. Brinza, who implemented the experimental test programs.

1. INTRODUCTION

The CAFB (Chemically Active Fluidized Bed) gasification process, in which limestone or dolomite removes the sulfur from fuel gas during the gasification process, was developed to permit the utilization of high-sulfur residual fuel oil or refinery bottoms in conventional boilers by producing a low-sulfur fuel gas. Coal is also being investigated as a fuel. The process can be operated as a once-through, limestone sorbent system, a sorbent regeneration/sulfur recovery system, or a sorbent regeneration system without sulfur recovery by capturing the sulfur-rich gas from the regenerator with the spent stone. The spent stone from each system alternative can be processed to minimize the environmental impact of the waste stone for disposal or to provide material for potential market utilization.[3,4]

Under contract to the U. S. Environmental Protection Agency (EPA), Westinghouse has carried out system analyses and laboratory support work on sulfur removal, solids transport, processing of spent sorbent for disposal or utilization, and the environmental impact of processed and unprocessed residue disposal.[3,4] Esso Research Centre, Abingdon, UK (ERCA) has carried out pilot-scale tests to investigate sulfur removal.[5] At San Benito, Texas, a 10 MW demonstration plant has been retrofitted by Foster Wheeler Energy Corporation and Central Power and Light Co. and is being tested.[6]

Work was performed to assess the potential market applications, to develop a basis for calcium-based sulfur sorbent selection, to determine the potential for alternative sulfur sorbents, to evaluate particulate control requirements, to identify and compare spent sorbent processing options, and to determine the environmental impact of the disposal of spent calcium-based sulfur sorbents. The results of this work has been reported and provides the basis for the engineering evaluation.

2. SUMMARY AND CONCLUSIONS

MARKET

Oil and gas represent about 30 percent of today's electric generating capacity, and the Fuel Use Act of 1978 precludes the use of oil and natural gas for existing plants after 1990. Many technology options exist for using coal, low-grade fuels, or alternative energy supply-and-demand technologies; and many international, institutional, and legislative actions will affect the choices to be made. This market assessment was carried out by evaluating the present CAFB concept within the present energy environment.

The CAFB process was conceived and designed for liquid fuels. The CAFB demonstration plant[6] is scheduled to carry out tests with residua and lignite fuels. The performance of the present CAFB configuration using solid fuel will provide perspective on the ability of the present concept to achieve required efficiency and environmental objectives. Our evaluation indicates that the CAFB configuration will require modification to achieve these objectives with solid fuels. After modification of the present CAFB configuration to process solid fuels, further evaluation would be required to include comparisons with other fluidized-bed processes designed for the gasification of solid fuels. The market assessment considers both liquid and solid fuels. Demonstration plant tests with lignite will provide further information that will result in clarification of the present conclusions:

- High-sulfur vacuum bottoms containing high-metal organic complexes and produced from vacuum distillation of atmospheric residual oil remain the most attractive fuel for the CAFB process.
- The availability of high-sulfur residual oil for CAFB processing is decreasing.

- Solid feedstocks such as lignite, tire scrap, or wood refuse are attractive fuel options; efficient utilization is projected to require design modifications in the present configuration, which was conceived for liquid fuels; demonstration plant tests are planned to determine performance with lignite.
- The potential utility capacity exceeds 100,000 MW; implementation will depend on the availability of suitable feedstocks; unless the concept is modified for solid fuel application that availability will be low.
- The generation of steam within a petroleum refinery is the most promising industrial application for the CAFB process; only the availability of residual fuels will limit the market.

SULFUR REMOVAL

- Sorbent selection will be determined by the attrition characteristics of the sorbent and its cost.
- A test apparatus and procedure was developed and demonstrated to compare sorbent attrition tendency; the mechanisms include calcination, thermal shock, grid jets, bubbling bed, and freeboard phenomena.
- Brownwood limestone was compared with three reference sorbents to assess its attrition tendency.
- Brownwood limestone, selected for the demonstration plant, is acceptable for regenerative operation; preliminary tests indicate air oxidation of the spent sorbent from once-through operation would not result in an environmentally acceptable material for direct disposal.
- Zinc oxide (ZnO) is the most attractive alternative sorbent for in-situ desulfurization in a CAFB gasifier based on thermodynamics.
- Iron oxide (FeO) could be used for external desulfurization.

PARTICULATE CONTROL

- CAFB liquid fuel gasification is expected to require conventional cyclones before and after the boiler to meet emission standards.
- Lignite gasification is expected to require conventional cyclones before the boiler and electrostatic precipitators or filters for final control.

3. RECOMMENDATIONS

Fluidized-bed gasification technology can be utilized to process residual oil, coal, or other low-grade fuels to produce a fuel gas for industrial or utility applications. This report has reviewed the capability of a specific fluidized-bed concept, the CAFB process. The following areas are recommended for further study and investigation in order to determine the capability of the CAFB process.

- Review the market potential following the scheduled demonstration plant tests using lignite. Available data support application of the technology to low-grade petroleum liquids. Our evaluation indicates, however, that the present CAFB configuration will require modification if it is to utilize solid fuels. This would limit the market potential, and it is thus important to understand and evaluate the scheduled lignite test results.
- Continue development work on the high-temperature sulfur removal system. This work has broad application (the CAFB process, designed for liquid fuels alternative gasification processes using "hot" gas cleaning, and fluidized-bed combustion processes, e.g., selected regenerative FBC and PFBC concepts) and merits further development. Specifically:
  - Continue development work on the processing of spent limestone sorbent from the regenerative process for disposal and utilization. Options recommended include dry sulfation, direct disposal, and briquetting.
  - Investigate methods for air oxidation of once-through calcium-based sulfur sorbents to achieve a material acceptable for disposal or utilization.
  - Continue development of alternative sulfur sorbents applicable to CAFB and other gasification processes - ZnO and FeO.

4. MARKET

It was clear when EPA began CAFB development work several years ago that a process to produce a clean, hot, fuel gas from high-sulfur residua (atmospheric or vacuum) had substantial potential. At that time

- Sulfur dioxide (SO_2) emission regulations were in effect and stricter regulations were planned, so combustion of high-sulfur residua required some provision for emission control.
- Residua hydrodesulfurization was (and is) expensive.
- Natural gas supplies were shrinking rapidly due largely to federal price controls, and many gas-fired boilers were going to be either shut down or switched to oil firing.

Thus, a clear path to CAFB commercialization was the use of a non-compliance fuel, high-sulfur residua, to feed a CAFB retrofit onto either a residua-fired boiler capable of gas firing or a gas-fired boiler. That path became even clearer in 1975 when Foster Wheeler developed interest in a Central Power & Light 10 MW CAFB retrofit on a San Benito, Texas, utility boiler,[7] and the Texas Railroad Commission issued a directive,[8] since rescinded, to Texas utilities in December of 1975 to schedule large reductions in natural gas consumption for power generation. This section will examine two aspects of what has happened since 1975 to that apparent market for CAFB: fuels and applications.

FUELS

Clean, low-sulfur fuels were never proposed for CAFB processing because they were suitable for direct combustion, i.e., they were in compliance with EPA requirements. High-sulfur oils that contained

nitrogen compounds and usually heavy-metal organic complexes, however, were proposed for CAFB processing. As listed in Table 5 of Volume I of our March 1975 report,[3] those fuels were either high-sulfur residual oil produced from atmospheric distillation of sour crude or high-sulfur vacuum bottoms produced from vacuum distillation of atmospheric residual oil. We concluded in the 1975 feedstock assessment that atmospheric residual oil would not be imported for a CAFB application because of a national need to minimize oil imports. That position has been strengthened considerably since 1975. Another conclusion in the 1975 assessment, that high-sulfur crude oil was not likely to be a CAFB feedstock, has also been strengthened since 1975. The recent "brink of disaster" situation regarding gasoline and home heating oil production in the United States due to shrinking domestic crude oil supplies and the ceiling imposed on oil importation absolutely dictates that all crude oil and atmospheric residual oil be processed by domestic refiners for distillate fuel production. Thus, the only CAFB feedstock possible from those mentioned in the 1975 assessment is high-sulfur vacuum bottoms.

Since 1975, other feedstock possibilities have developed. Foster Wheeler has proposed coal, particularly lignite, as a feedstock for the San Benito and other CAFB units.[6] Also, the burgeoning synfuels program in the U.S. raises the possibility of coal- or oil-shale-derived liquid feedstocks for CAFB. Finally, wastes and refuse from pulp and paper, petrochemical and plastics plants, and scrap rubber have been proposed. Recently, the price decontrol of heavy crude oils (16° API gravity or lower) also raised the possibility of an increased quantity of vacuum bottoms derived from refining these heavy crudes.

In order to assess the use of the possible CAFB feedstocks just mentioned, two principal considerations need to be addressed, availability and suitability.

Availability of Fossil Fuels

Recent discussions with oil refinery architect/engineering firms and with synfuel project sponsors have provided insight into the

probability of utilization of shale oil, coal-derived oil, or heavy crude refining residua for a CAFB unit. Also, recent pronouncements from the legislative and executive branches of the federal government indicated the direction of future political action.

A continuing transportation fuel (gasoline, jet fuel, and diesel fuel) squeeze is projected for the domestic market. We must, for reasons of national security and a sound economy, decrease our dependence on imported oil on the one hand, and, on the other, increasingly obtain these distillate fuels (plus home heating oil and domestic combustion turbine peaking fuel) from declining domestic sources. The efforts to do so have a common drawback. Distillate fuels contain more hydrogen than the raw materials (heavy crude oil, oil shale, or coal), from which they must be derived. That hydrogen deficiency, plus the increased need for hydrogen to desulfurize or denitrogenate the sour crudes and syncrudes that will make up a growing percentage of our domestic supply, places a substantial new demand on domestic hydrogen supply. The hydrogen, wherever possible, will be supplied by residua from the refining operation through partial oxidation, either in a Shell/Texaco-type partial oxidation system or in a fluid coking/Flexicoking-type system. The ash-containing residual materials from direct liquefaction of coal will also be consumed in hydrogen production. Present plans of the developers of H-Coal, SRC-II, Exxon Donor Solvent, and COGAS processes indicate that all ash-containing material will probably be used for hydrogen generation in oxygen-blown gasification units. Tar sands operations will use the residual as coker feedstocks and use the low-sulfur coke as boiler fuel for raising steam to be used in the tar/sand separation. Oil-shale-derived oils will require denitrification from hydrogen produced via partial oxidation of residua. Heavy oil refining will, in turn, require more fuel and more hydrogen for upgrading the reformer and cat cracker feed streams and will consume the high yields of residua to produce that fuel and hydrogen. CAFB is not presently designed for such hydrogen production.

Politically, restrictions on imports of oil plus the increasing demand by third world nations[9] for distillate fuels, which is shrinking the supply of residua from the Caribbean area, and the pressure by the Department of Energy (DOE) for utilities to convert boilers from oil to coal and to natural gas all indicate shrinking availability of residua for CAFB processing for utility applications.

Alternative Fuels

While the CAFB was proposed for gasification of high-sulfur residua, other nonfossil fuels are available.

The following abstracts and titles have been reviewed to identify alternative fuels:

- Engineering Index (manual search) Abstracts 1974-1976
- Appl. Sci. & Tech Index (manual search) Titles 1974-1976
- Engineering Index (Lockheed computer search) Abstracts 1970-1976
- Chemical Abstracts (Lockheed computer search) Abstracts 1970-1976
- EPA Solid Waste Int. Retrieval Service (computer) Abstracts 1970-1976

This search yielded about 400 references and abstracts describing fluidized-bed gasification, pyrolysis, and incineration.

Waste fuels that have been identified for gasification, pyrolysis, or incineration are listed below.

The extensiveness of this list suggests that practically any burnable waste may potentially be incinerated or gasified in a fluidized-bed process such as CAFB. Some wastes such as sewage sludge are very wet, while others such as waste plastic are very dry.

Alternative Fuels

Bark
Groundwood mill sludge
Kraftmill sludge
Paint sludge
Rubber waste
PVC
Municipal refuse
Vinyl chloride monomer
Ore sludges
Mixed plastics (PE, PP, PS)
Polyethylene
Sewage sludge
Plastics from municipal refuse
Manure
Tires
Sawdust, peanut shells, rice husks
Coal washery rejects
Refinery waste
Agricultural & forestry waste
Distillery slops, packing-house waste

It seems that the fuels best suited to the CAFB are those that are rich in sulfur and that will exploit the sulfur-capturing potential of the process. The sulfurous fuels include rubber tires (0.95 to 1.1 wt % sulfur), rubber scrap (about 2% sulfur), sulfide-containing wood-digestion liquors, and coal washery rejects. There are, in addition, vast stores of obsolete chemical munitions stored in the USA containing over 300 million pounds of toxic fill (TRW, VII, p 255, XIV, p 153). Some of these are sulfur compounds, such as sulfur mustard $(ClCH_2CH_2)_2S$, for which the recommended disposal method is incineration. Such obsolete munitions may well be suited to destruction in the CAFB along with recovery of useful energy and control of sulfur emissions.

Suitability

The CAFB process as presently configured was not designed to use the solid feedstocks proposed as possible fuels, such as lignite, tire scrap, or wood refuse. Tests planned at the San Benito, Texas demonstration plant will provide perspective on performance with lignite.[6]

The liquid residua feedstocks are suitable (but as discussed above will be increasingly unavailable). Their suitability stems from the gasification mechanism proposed by ERCA:[4]

> In the shallow fluidised bed of the gasifier there is a rapid circulation of lime between top and bottom. Indications are that coke is laid down on the lime in the upper portion of the fluid bed by oil cracking and coking reactions and that this coke burns off in the lower portion where oxygen is supplied by the air distributor.

Oil as a feedstock permits this coke laydown on the circulating limestone; solids feedstocks such as lignite do not. Instead, lignite is present at a high concentration in the gasifier bed to maintain an adequate gasification rate and is fed at that concentration from the gasifier to the regenerator. The concentration of unreacted fuel fed to the regenerator, therefore, is much higher for lignite than for oil gasification. As a result, proper regeneration of sulfided stone may not be achieved because of the high heat release from the reaction of the air in the regenerator with unreacted lignite. This difficulty has not yet been overcome by the CAFB unit at Abingdon or by the plant at San Benito, and until it is, we cannot say that solid feedstocks are suitable for CAFB processing.

These constraints on the availability and suitability of fuels for CAFB indicate, at best, a very restricted market based on special local conditions that may make a residuum available for a sufficient time to justify a CAFB investment. Generally, such an availability of a suitable feedstock for the present configuration cannot be expected in the forseeable future in the U.S. Modifications to the concept to permit utilization of solid fuels would extend the feedstock availability.

UTILITY APPLICATIONS FOR THE CAFB PROCESS

Development of the CAFB has been devoted almost entirely to the atmospheric pressure operation of the process. At atmospheric pressure

the CAFB is suitable for providing low-heating-value gas to a conventional utility boiler. The feasibility of operating the CAFB at pressures suitable for combined-cycle power generation has previously been evaluated.[10] These two utility applications of CAFB are influenced by several market factors.

Atmospheric Pressure CAFB

As mentioned briefly earlier, the use of a CAFB retrofit to a gas-/oil-fired boiler has been its most likely application. The present U.S. policy of conversion away from oil to coal or to the newly plentiful deregulated natural gas or even to nuclear* has an obvious effect on a process designed to use oil, even high-sulfur, high-heavy-metals-content vacuum bottoms oil.

Potential utility sites for a CAFB retrofit are abundant. A survey of the gas-fired utility boilers (nearly 85 percent of which can also fire oil) installed in the 48 contiguous states can be summarized as follows:

Year Commissioned	Total MW
1978	516
1977	1,191
1976	2,686
1975	2,878
1974	5,014
1973	5,286
1972	4,531
1971	5,356
1970	4,280
1969	2,650
1968	3,462
1967	6,007

*(President Carter in his announcement of a new NRC Chairman on Dec. 7, 1979).

Year Commissioned	Total MW
1966	4,479
1965	2,771
1964	3,465
1963	3,325
1962	2,042
1961	3,104
1960	2,742
1959	3,216
1958	3,201
Pre-1958	33,360
TOTAL	105,562

The preponderance of this capacity is in the "sunbelt": southern California, Nevada, Arizona, New Mexico, Texas, Louisiana, Mississippi, and Florida; and essentially all of the capacity commissioned since 1958 has gas/oil capability. The gas-only units are mostly small, pre-1950 installations, many of which are retired or are on peaking service. The utility groups, such as the Florida Operating Group, Middle South Utilities, Texas Utilities Companies, the SCEC Power Pool, and the California-Nevada Area Group, account for a large majority of the capacity listed. These utility groups are in the region where population growth is pressuring the utilities to continue to expand generation capacity. Admittedly, there are no new, gas-fired units scheduled to come on line in the future due to the severe gas shortage in the mid-1970s, but the point is that all of the gas-fired utility capability installed since 1958 must be under pressure to continue power generation. The question is, will this need be assisted by CAFB retrofit?

The answer to that question is a matter of fuel supply, timing, and economics. The fuel supply was discussed in the preceding section. Presently, the supply of fuel is dominated by a sharply increased

natural gas supply. The "gas bubble" is certainly a transient phenomenon. But how transient? The American Gas Association, in its publication, A.G.A. Monthly, has been indicating at least five years and probably ten years as the forseeable duration of the bubble. Lower-48 gas production will be nearly 5 trillion ft^3/yr higher in 1990 due to deregulation than was projected under Federal Price Control.[11] Also, agreements with Mexico for supply from their large and expanding gas fields, plus future supplies of gas from Alaska, to take the pressure off the southwestern U.S. supply of gas, indicate that the natural-gas-fired utility boilers could remain natural-gas-fired for about another decade. After 1990, CAFB may have available to it some of the 70^+ GW of, by then, 20-to-30-year-old units for retrofit. Our opinion, as presented in the preceding section, is that the general likelihood then of suitable feedstocks being available for CAFB after 1990 is low, possibly a special situation here or there, but no more than that.

The industrial boiler situation is similar. The AGA recognizes that eventually natural gas will be too scarce a domestic resource to permit utility boilers to burn it; thus, the projected availability of utility boilers to CAFB retrofit in the 1990s. The industrial market, however, is one that the gas industry is presently actively promoting for installation of new capacity, all in the political guise of reducing oil imports and accompanied by a campaign to "enable states to classify dual-fuel customers to firm category (i.e., permit firm gas supply commitments to industry) recognizing environmental benefits of gas use."[12] The industrial oil offsets now available total over 700,000 bbl/day of imported oil, with a projection by AGA to nearly 1.2 million bbl/day in 1980! We see little possibility that industry, interested in low first cost, efficiency, and minimum environmental intrusion, will be persuaded to use a CAFB system in the forseeable future.

Previous assessment of the utility boiler population has shown that the coastal regions (Federal Power Commission regions I, III, V, and VIII) represent the areas of greatest interest to the CAFB with about

700 gas- and oil-fired boilers existing up to 1000 MWe in capacity.[3] FPC region I (the Northeast) is probably not applicable because of a trend to convert these boilers to the use of coal. Almost all of the boilers smaller than 50 MW_e (300 in number) are 20 to 40 years old and represent a market of limited applicability. The number of applicable boilers, between 50 and 400 MW_e in capacity, number about 300. They are also located in the regions of potentially greatest low-grade residual oil availability, if we assume a special local condition as discussed earlier.

The ability to retrofit these boilers with the CAFB is an important concern. A 50 MW_e CAFB demonstration plant design has shown that space in close proximity to the boiler may be very limited, requiring either very long, hot, low-heating-value fuel gas piping, or removal of equipment to provide space for the CAFB process.[3] Burners, hot air ductwork, windboxes, water walls, and I. D. fans may have to be modified. Two studies of boiler retrofit with cold, low-heating-value fuel gas generated by coal gasification indicate that a fuel gas having the characteristics of the CAFB fuel when fired in an extensively modified boiler could achieve the maximum rating of the boiler, but the modification could cost typically $14/kW for a boiler whose original design fuel is gas[13,14] (based on cold, low-heating-value fuel gas). The steam generator efficiency at maximum rating would also be reduced, and, if the original design fuel for the boiler were gas, the unit would no longer be capable of gas-firing. This is an area requiring further definition.

Pressurized Low-Grade Residual Oil Gasification

The gasification of low-grade residua at elevated pressures in a process similar to the atmospheric pressure CAFB can be used to supply low-heating-value gas to a highly efficient and economically attractive combined-cycle power plant.[15]

The pressurized CAFB operation should be carried out with dolomite as the preferred sorbent and can be operated with either sorbent regeneration by the steam/CO_2 reaction

$$CaS + CO_2 + H_2O \rightleftharpoons CaCO_3 + H_2S \quad ,$$

or with once-through sorbent utilization. The air regeneration scheme used with the atmospheric pressure CAFB process does not appear economically feasible at pressures suitable for combined-cycle operation.

The critical market factors influencing the pressurized oil gasification process are the availability of low-grade residual oils and the competing economics of alternative power generation techniques. The pressurized oil gasification process appears to be economically attractive when compared with alternative technology.[15] Low-grade residua oils will be no more available for the pressurized than for the atmospheric CAFB process (see FUELS section).

INDUSTRIAL APPLICATIONS FOR THE CAFB PROCESS

The development of the CAFB process has been directed toward the generation of steam using low-grade petroleum residua specifically for electric utility application. The potential for utilizing the CAFB low-heating-value fuel gas for industrial purposes - steam generation for process steam, process heating, or power generation; process direct or indirect heating; or process gas supply - has been assessed for the purpose of identifying alternative applications that should be developed.

The goal of applying the CAFB process industrially would be to reduce the industrial consumption of clean fuels, such as natural gas and distillate fuel oils, or to permit the utilization of low-grade petroleum residua that might already be consumed industrially in an environmentally acceptable manner. The feasibility of achieving this goal has been evaluated by a survey of U.S. industries - their energy consumption and process characteristics. A similar study has been carried out by Battelle for the industrial application of low- and intermediate-heating-value gas generated from coal.[16]

Limitations of the CAFB Process as an Industrial Low-Heating-Value Gas Generator

Characteristics of the CAFB process and industrial low-heating-value gas applications limit the applicability of the CAFB process:

- CAFB has been extensively tested only for low-grade petroleum residues. This limits fuel availability and restricts application to industries located in regions where these fuels may be available. In general, it would be inconsistent with national policy to substitute petroleum derivatives where coal is already in use.
- The CAFB low-heating-value gas is hot (~870°C) and would be difficult to cool because of its high tar content. Cooling would also reduce the system efficiency by 10 to 15 percent. Many industries supply a large number of process fuel needs by means of extensive gas or oil distribution systems. Cooling the CAFB gas would be required and/or replacement of the distribution system by an expensive, high-temperature gas distribution system. Also, because of space limitations, in many retrofit cases the CAFB gasifier may not be placed in close proximity to a single large user of the low-heating-value gas, again requiring cooling or expensive high-temperature piping.
- The CAFB is an atmospheric-pressure, operating-gas producer that cannot fill pressurized process gas requirements in its present state of development. Also, many existing fuel gas distribution systems are designed on the basis of natural gas delivering at ~345 kPa and could not carry a corresponding energy rate of low-heating-value gas even if it were cooled.
- The purity of the CAFB low-heating-value gas (containing particulate, tars, etc.) would not satisfy the constraints

of many process gas users. The flame temperature requirements of some industrial processes could not be supplied by the CAFB fuel gas.

- Many new-plant industrial applications such as steam generation or process heating could be satisfied by alternative techniques such as fluidized-bed combustion or conventional direct combustion of low-grade fuels with fuel gas cleaning. These techniques would probably be economically superior to the CAFB process.
- Many industrial boilers and process heaters may be incapable of retrofit to low-heating-value gas due to space constraints or they may suffer because of economics or performance.[13]

On the basis of these generalizations, we conclude that the CAFB could be applied economically only to industrial situations consisting of the retrofit of large existing steam generators (process steam, process heating steam, or power generation steam). Industries with large steam requirements that are presently supplied by clean fuels and are located in regions with potential low-grade petroleum fuel availability could be considered.

Industries Surveyed

Energy consumption, pollution characteristics, and process needs of the large U.S. industrial energy users were surveyed.[2,3,17] The six general industrial categories - food; paper; chemicals; petroleum and coal; stone, clay, and glass; and primary metals - represented 77 percent of the purchased energy consumed in manufacturing in 1967.

Table 1 indicates the 1967 energy consumption and energy intensity (1000 Btu energy consumed/$(1967) value added) of the major U.S. industries. The largest energy-consuming category is primary metals, which is led by blast furnaces and steel mills. The second highest consumer is the chemical industry. The most energy intensive major category is

petroleum and coal products at 284.38 (1,000 Btu/$(1967). Among the individual industries the lime industry is the most energy intensive. In addition to consuming purchased energy, several industries consume significant captive energy (raw materials that are converted to products and subsequently used to provide energy). The major consumers of captive energy are the petroleum industry and blast furnaces and steel mills.

Assessment

Because of process requirements and the availability of residual fuel oils the food and paper industries do not represent areas of potential CAFB application. The remaining four general industrial categories, however, do provide applications that satisfy some of the CAFB criteria.

The chemical industries could utilize CAFB to supply the steam requirements for a large chemical complex. Two factors will limit the applicability to the chemical industries: the availability of residual fuel oil and the feasibility of retrofiting existing steam generators with the CAFB process. Only chemical plants located in regions of high potential residual oil availability could be considered. This would probably limit interest to U.S. coastal regions (PADs I, III, and V)[18] for the chemical industries or most other industrial application. Small chemical plants with small steam utilization rates or large chemical plants with numerous small steam generators distributed within the complex are probably not of interest. The distribution of steam generator sizes in U.S. chemical plants is unknown.

The criteria for the CAFB process may be most clearly satisfied in the petroleum refining industry. Table 2 summarizes the energy consumption by fuel source for petroleum refining. Large amounts of natural gas are consumed by refineries, while large amounts of captive energy are available in the form of residual oil, petroleum coke, and refinery (still) gas. Large steam generators present in refineries should be capable of CAFB retrofit, but, again, space may be limiting.

Table 1

GROSS ENERGY PURCHASED COMPARED WITH SHIPMENTS AND VALUE ADDED, HIGH-ENERGY-USING MANUFACTURING INDUSTRIES, 1967

		Gross energy (trillion BTUs)	Shipments (million 1967 $)	Ratio gross energy to shipments (1)(2) (1,000 BTUs/ 1967 $)	Value added (million 1967 $)	Ratio gross energy to value added (1)(4) (1,000 BTUs/ 1967 $)
		(1)	(2)	(3)	(4)	(5)
All manufacturing		15,683.3	557,398	27.74	261,984	59.02
20	Food and kindred products	1,097.7	83,972	13.07	26,620	41.24
2011	Meatpacking plants	101.6	15,576	6.52	2,220	45.75
2026	Fluid milk	81.5	7,826	10.41	2,351	34.67
2033	Canned fruits and vegetables	58.3	3,468	15.65	1,413	38.42
2037	Frozen fruits and vegetables	36.4	2,082	17.50	784	47.66
2062	Prepared feeds	59.7	4,797	12.44	1,227	48.66
2051	Bread, cake, and related products	59.1	5,103	11.59	2,753	21.47
26	Paper and allied products	1,367.0	20,970	65.19	9,756	140.11
2611	Pulp mills	98.0	730	134.27	334	293.48
2621	Paper mills except building paper	603.2	4,844	124.52	2,356	255.99
2631	Paperboard mills	476.9	2,907	164.05	1,509	316.08
2653	Corrugated and solid fiber boxes	36.3	2,960	12.28	1,130	32.12
2661	Building paper and board mills	49.9	361	146.32	184	271.64
28	Chemicals and allied products	1,257.1	42,168	77.28	23,550	138.31
2812	Alkalies and chlorine	266.9	720	370.76	419	636.69
2813	Industrial gases	112.3	589	190.61	401	280.12
2815	Cyclic intermediates and crudes	149.8	1,597	93.79	730	205.35
2818	Industrial organic chemicals, n.e.c.	952.1	6,378	149.27	3,575	266.30
2819	Industrial inorganic chemicals, n.e.c.	971.3	4,248	228.66	2,295	423.13
2821	Plastic materials and resins	180.9	3,974	46.04	1,535	97.83
2822	Synthetic rubber	71.6	917	11.19	406	196.31
2823	Cellulosic man-made fibers	100.8	903	111.44	507	198.90
2824	Organic fibers, noncellulosic	107.4	2,033	52.83	1,232	85.80
29	Petroleum and coal products	1,543.0	22,063	70.00	5,426	284.38
2911	Petroleum refining	1,459.2	20,294	71.90	4,765	307.52
32	Stone, clay, and glass products	1,361.0	16,469	92.81	8,333	160.93
3211	Flat glass	60.5	611	99.10	423	143.06
3221	Glass containers	135.5	1,352	100.21	842	160.89
3229	Pressed and blown glass, n.e.c.	74.1	886	83.62	659	112.46
3241	Hydraulic cement	515.2	1,266	813.65	812	634.25
3251	Brick and structural clay tile	101.6	362	280.72	251	404.62
3273	Ready-mixed concrete	41.3	2,684	15.39	1,156	35.73
3274	Lime	81.9	176	465.44	100	818.18
33	Primary metal industries	3,339.9	46,731	71.47	19,978	167.18
3312	Blast furnaces and steel mills	1,810.6	19,621	92.28	8,910	203.21
3313	Electrometallurgical products	131.0	468	280.02	193	678.05
3321	Gray iron foundries	118.8	2,638	45.03	1,543	76.99
3323	Steel foundries	55.5	1,213	45.78	791	70.12
3334	Primary aluminum	589.4	1,609	366.31	812	720.04
3351	Copper rolling and drawing	43.7	2,391	18.28	706	62.04
3352	Aluminum rolling and drawing	96.0	2,959	32.45	939	102.27
3357	Nonferrous wire-drawing, insulating	37.9	3,591	10.56	1,330	28.49
3391	Iron and steel forgings	58.7	1,262	46.53	607	96.66

Sources: Energy: Ready-mixed concrete (SIC 3273)--Table 22.1. All other industries--like "reported energy" in Table 1.1 (with correction of a typographical error in fuel oil purchases by iron and steel forgings, SIC 3391). Shipments and value added: U.S. Bureau of the Census, Census of Manufactures, 1967, Volume II, part 1, table 3.

petroleum and coal products at 284.38 (1,000 Btu/$(1967). Among the individual industries the lime industry is the most energy intensive. In addition to consuming purchased energy, several industries consume significant captive energy (raw materials that are converted to products and subsequently used to provide energy). The major consumers of captive energy are the petroleum industry and blast furnaces and steel mills.

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Table 2

PETROLEUM REFINING CENSUS DATA: USEFUL ENERGY BY MAJOR SOURCE, 1958 TO 1967[17]

Energy Sources	1958	1962	1967
	In Physical Units		
Purchased			
Coal, million short tons	1.069	.789	.777
Petroleum, million bbls.	1.933	7.334	7.263
Gas, billion ft^3	783.694	942.488	1,100.756
Other fuels, $ million*	7.300	11.200	20.600
Electric energy, billion kWh	9.115	12.147	17.474
Captive Consumption			
Residual oil, million bbls.	43.147	34.582	41.638
Other fuels, incl. petroleum coke million bbls.	17.415	40.827	42.055
Refinery (still) gas, billion ft^3	676.970	776.351	714.568
	In Trillions of Btus		
Total Energy	2,093	2,283	2,508
Purchased	904	1,115	1,336
Coal	28	20	20
Petroleum	11	43	42
Gas	811	975	1,139
Other Fuels*	23	35	76
Electric energy	31	41	60
Captive Consumption	1,033	1,189	1,172
Residual oil	271	217	262
Other fuels, incl. petroleum coke	82	192	198
Refinery (still) gas	680	780	711

*Includes gasoline, LPG, wood and purchased steam, and fuels not specified by kind.

Source: Bureau of the Census, Census of Manufactures, Fuels and Electric Energy Consumed, 1967.

Stone, clay, and glass product industries do not appear to be promising applications for CAFB. The highest energy user in this classification, hydraulic cement, consumes most of its energy in firing rotating kilns. These kilns are capable of direct coal firing, and retrofit by CAFB fuel gas may not be feasible. The most energy-intensive industry in this industrial category, the lime industry, is a large user of coal, coke and breeze, and natural gas but uses very little fuel oil as shown in Table 3. Most of the energy consumption in the glass industry requires high flame temperatures which would limit the applicability of the CAFB fuel gas.

The primary metal industries fail to satisfy the criteria for CAFB application. Blast furnaces and steel mills, which are the higher energy consumers in this category, are also large consumers of captive energy in the form of coke, breeze, blast furnace and coke oven gas (Table 4). Residual oil would have very limited applicability in this industry. The secondary steel industry, which does not have available to it the captive energy of the integrated mills, could use a low-heating-value gas for furnace operations of heat-treating and forming where presently natural gas is used.[17] We expect this application to be unsuitable for CAFB because of extensive gas distribution and furnace modification problems.

The primary aluminum industry is a large consumer of electrical energy, some natural gas, and almost no residual oil (Table 5). Because of its high electrical energy consumption the primary aluminum industry is located in regions of cheap hydroelectric energy where residual oil is generally unavailable.

Conclusions

The single most promising alternative application for the CAFB process is the generation of steam within a petroleum refinery. No other alternative applications have been identified, although others may exist in special circumstances. Also, alternative applications may become

Table 3

LIME INDUSTRY DISTRIBUTION OF ENERGY UTILIZATION, BY SOURCE
(trillion Btu, and percentages)[17]

	1947	1954	1958	1962	1967
Coal, Coke, & Breeze	44.6 (78.4)	35.2 (63.0)	29.4 (56.0)	39.6 (64.5)	42.0 (51.3)
Fuel Oil (total)	1.9 (3.3)	2.4 (4.3)	1.7 (3.2)	1.8 (2.9)	2.3 (2.9)
Gas	6.0 (10.5)	14.5 (25.9)	15.9 (30.3)	15.7 (25.6)	31.1 (38.0)
Other Fuels & Fuels n.s.k . .	1.2 (2.1)	0.5 (0.9)	2.2 (4.2)	0.5 (0.8)	1.2 (1.0)
Electric Energy (gross energy consumed basis)	3.0 (5.7)	3.3 (5.9)	3.3 (6.3)	3.7 (6.2)	5.3 (6.9)
Electric Energy (useful energy)	0.7	0.9	1.0	1.2	1.7
Total (gross energy consumed basis)	56.9 (100)	55.9 (100)	52.5 (100)	61.4 (100)	81.9 (100)
Total (useful energy)	54.5	53.5	50.2	58.9	78.3

Note: Figures in parentheses represent percentage distribution of total which is based on gross energy consumption.

Table 4

BLAST FURNACES AND STEEL MILLS CENSUS DATA: ENERGY UTILIZATION 1958-1971, (Trillion Btu) BY MAJOR ENERGY SOURCE[17]

Energy Source	1958	1962	1967	1971
Useful Energy	2,423	2,768	3,223	n.a.
Purchased	1,143	1,471	1,566	1,472
Coal	174	178	148	131
Coke	293	364	286	266
Petroleum	211	200	179	161
Gas	374	616	748	655
Other fuels*	30	36	44	93
Fuels, n.s.k.**	5	n.a.	43	8
Electric energy	56	77	119	158
Captive consumption	1,280	1,297	1,657	n.a.
Coke & breeze	942	993	1,236	n.a.
Blast furnace & coke oven gas***	338	304	421	n.a.
Gross Energy	2,548	2,930	3,467	n.a.
Purchased	1,268	1,633	1,810	1,802
Captive consumption	1,280	1,297	1,657	n.a.

Estimates based on Bureau of the Census data.
*Includes gasoline, LPG, wood and purchased steam.
**Fuels not specified by kind.
***Blast furnace gas is a coke by-product and included in the coke energy.
n.a. - not available.

Table 5

ALUMINUM, ESTIMATED U.S. INDUSTRY SOURCES AND USES OF ENERGY, 1971
(data are (10^{12}) Btu except as marked)[17]

	Alumina Refining	Anode Baking	Smelting	Fabrication	Vehicles	Other	Total energy by type	
								Percentage
Electricity	18.3	*	665.9	94.0	-	-	778.2	79.8%
Coal	-	-	-	6.9	-	-	6.9	0.7
Distillate oil	-	*	-	3.2	0.1	0.1	3.4	0.3
Residual oil	0.8	-	-	1.6	-	-	2.4	0.2
Gas	75.1	5.8	-	88.3	*	1.9	171.2	17.5
LPG	*	*	-	6.0	2.6	-	8.7	0.9
Gasoline	-	-	-	-	4.6	-	4.6	0.5
Total energy by use	94.2	6.0	665.9	200.0	7.4	2.0	975.5	-
Percentage	9.7%	0.6%	68.3%	20.5%	0.8%	0.2%	-	100%

Note: Distribution of data along the columns is based on proportions derived from Table 31-1. Data exclude fuel usage in production of alumina not sold to aluminum with the difference being taken from gas row. This single deduction is made on the assumption that the difference lies primarily in calcining alumina.

*Denotes less than 0.05(10^{12}) Btu.

apparent when it is demonstrated that alternative fuels such as municipal wastes, industrial wastes, or coal can be utilized by the CAFB.

Constraints on the availability and suitability of fuels for CAFB indicate, at best, a very restricted market based on special local conditions that may make a residuum available for a time sufficient to justify a CAFB investment. Generally, such availability of a suitable feedstock cannot be expected in the U.S. in the forseeable future.

5. SULFUR REMOVAL

CALCIUM-BASED SORBENTS

The desulfurizing action of the CAFB process is usually represented by the chemical reaction:

$$CaO + H_2S \longrightarrow CaS + H_2O \quad .$$

The apparent simplicity of the process conceals the complex mechanism of interaction between the fuel sulfur and the calcium-based sorbent as oil is converted into a low-sulfur fuel gas. Thermodynamically, the equilibrium for the reaction lies far to the right and predicts >95 percent sulfur capture. Kinetic effects, process conditions, and the physical and chemical state of the calcium sorbent, however, are dominant in determining the extent of sulfur capture. Sorbent stone type, particle size, the previous thermal and chemical history of the sorbent, and its mechanical strength all influence the desulfurizing effectiveness of the process and its operability. ERCA, for example, found one sorbent - Conklin limestone - to be impossible for use in a fluidized bed because of the high rate of attrition and elutriation of the stone as it was fed to the gasifier.[19] The large variety of potential calcium-based sorbents (e.g., limestone, dolomite, impure limestone, marble, aragonite, marl) make it necessary to develop sorbent specifications from the available data and to devise screening methods by which the suitability of a particular candidate material can be assessed.

The relevant data come essentially from three sources:

- The operating experience of ERCA on the continuous pilot plant and on the batch gasifiers at Abingdon[5]
- The laboratory tests and data assimilation carried out by Westinghouse for the CAFB process evaluation[3]

- The laboratory tests and fluidized-bed work on other sulfur-removal systems using calcium-based sorbents carried out by Westinghouse and other contributors (Exxon, Argonne National Laboratories [ANL], Consolidated Coal [CONOCO], Foster-Wheeler [FW], Pope, Evans and Robbins [PER], and Combustion Power) on programs for EPA and DOE.

The suitability of a particular sorbent can be defined in an idealized manner. If a sorbent has a sufficiently high reaction rate with the liberated fuel sulfur under the process conditions, it should effectively desulfurize the fuel gas. Westinghouse has measured the reaction rate of several stones with hydrogen sulfide (H_2S) in a fuel gas using a thermogravimetric apparatus (TGA); in all cases the reaction rate has been sufficiently fast to capture 90 percent of the fuel sulfur, according to the predictions of a model of fluidized-bed desulfurization applied to CAFB operating conditions.[3] None of the stones tested showed a marked difference in reaction rate below 30 percent utilization of the calcium fraction in the stone. These results lead to three general conclusions:

- The sulfur removal capability of different stones should be similar at low calcium utilization (<30 percent).
- The sulfur removal should improve as the bed height is increased.
- The sulfur removal should be high (>90 percent) at calcium-to-sulfur (Ca/S) feed rates as low as 3/1.

The operating experience of ERCA[5] can be compared with predictions from laboratory studies. In batch studies, at a Ca/S makeup rate of 1.5 to 1.6, the sulfur removal efficiency for three stones (BCR 1691, Denbighshire, and BCR 1350) was 75, 76, and 76 percent. At Ca/S makeup rates of 2.83 and 2.71, the sulfur retention for BCR 1359 and Pfizer calcite (Adams, MA) was 89 percent. These results apparently show that sulfur removal is independent of the type of stone used; but ERCA, in evaluating the effect of variation in the run conditions, concluded

that Denbighshire was the superior sorbent, the remaining three being equally active. Later tests, however, showed that Limestone 1359 was marginally better than Denbighshire. It seems probable that there is indeed, no difference in the inherent sulfur removal ability of the sorbents tested and that slight changes in operating conditions are responsible for the differences noted.

Other tests by ERCA have shown that sulfur removal is improved very little by increasing the bed depth; further, the Ca/S mole ratio has always been much higher than 3/1 when high sulfur removal efficiencies were achieved. Later test runs did show, however, that a deeper bed gave greater sulfur removal. Recent evidence suggests that the sulfur is not entirely released as H_2S and that organic sulfur compounds in tars escape from the bed of lime. Hydrogen sulfide introduced into the bed is efficiently fixed by the lime, a result that agrees with fluidized-bed studies of lime sulfidation at Westinghouse.

Although testing of a candidate sorbent will give information on its reactivity with H_2S, high reactivity does not ensure successful operability of the process with a particular stone. Other factors, such as stone attrition, fines recirculation, and air injection, may be dominant in controlling the desulfurizing action.

Development of Sorbent Selection Criteria

Westinghouse has carried out sorbent selection studies for a CAFB demonstration plant site in Providence, Rhode Island.[3]

This evaluation of the relevant data has led to the definition of stone selection criteria based on:

- Acceptor properties of the stone for sulfur removal
- Attrition resistance of the stone
- Trace element emission characteristics
- Regeneration characteristics
- Suitability of spent sorbent for final processing for disposal

- Economic availability of the stone.

A change in the demonstration plant site to San Benito, Texas mandated that limestones available in the Texas area be assessed for their suitability in the CAFB process.

Limestone from Texas and Mexico were evaluated as candidate sulfur sorbents for the CAFB gasification demonstration plant at San Benito. The procedure followed was to identify candidate stones using available literature and expertise on the limestone industry in the area surrounding San Benito. Attrition was measured by elutriation losses suffered by samples of these stones in a small fluidized-bed unit under calcination conditions. The samples were evaluated for their reactivity to H_2S in a fuel gas mixture at 870°C. Trace element analyses of the minerals were carried out. This test procedure left unclear the distinctions between most of the stones tested, and it was recommended that the cost of the sorbent determine the choice.

A separate topical report[20] was issued describing the results of the sorbent selection study for the CAFB demonstration plant.

Brownwood Limestone Tests

The sorbent selected by FW for the La Palma demonstration plant, Brownwood limestone, was evaluated. The received size distribution was determined and the sulfur removal performance of the composite distribution obtained from TG sulfidation tests on nine size fractions of the sorbent. The possible deactivation of the sorbent during prolonged exposure to high temperatures and the feasibility of oxidizing sulfided Brownwood limestone in air for disposal in the sulfated form were examined.

Experimental Procedure

The reaction rate of limestone with H_2S was determined in a modified Du Pont thermogravimetric reactor. A 20-mg sample of double-screened limestone was suspended from the balance arm in a platinum mesh

basket. A sheathed, chromel-alumel thermocouple, located about 1 cm above the sample, measured the nominal sample temperature. The sample was heated to temperature at a programed rate of 10°C/min. After complete calcination, 0.5 percent H_2S in a fuel gas mixture (2.5% CH_4, 10% CO, 25% H_2, 16.4% CO_2, N_2) flowing at 600 ml/min (STP) was introduced. The fraction of calcium sulfided was monitored, with time, by the weight change of the sample.

Experimental Results

Brownwood Limestone Sulfidation. The analyses made on Brownwood limestone are summarized in Table 6.

Sulfidation tests on Brownwood limestone were carried out on nine particle size fractions. The particle size distribution received consisted of fairly large particles, more than 50 percent of them larger than 3000 μm. The coarse particles, however, were extremely reactive. Data from the tests were compounded (by a weight-averaging basis) to determine the sulfidation rate as a function of sorbent utilization for the material, as received. Figure 1 shows the rate of reaction obtained for the 2380 to 3360 μm (6 to 8 mesh) size fraction and the composite rate curve for the as-received material.

A simple model developed for desulfurization in fluidized beds[21,22] can be used to estimate Ca/S molar feed requirements for desulfurization in once-through processes, using rate constants derived from TG data. The model projections have agreed very well with fluidized-bed combustor pilot plant data.[22] The use of the model for desulfurization projections for the CAFB process however, requires that the sulfur be in the form of H_2S. The ability of the limestone to absorb organic sulfur is unknown.

For 85 percent desulfurization in a 0.9 m bed fluidized at 1.4 m/s, the reaction rate required is shown in Figure 1. (The method of making the projections is detailed elsewhere.[22]) At this reaction rate with

Table 6

ANALYSIS OF BROWNWOOD LIMESTONE

- Chemical Analysis

Compound	% Weight
Ca as CaO	53.3
Mg as MgO	0.53
CO_2	43.6
Al as Al_2O_3	0.94
Fe as Fe_2O_3	0.97
Si as SiO_2	1.84
Na as Na_2O	0.026
K as K_2O	0.17
Cl	0.0032
Total	101.4
Ignition Wt. Loss, %	42.4

- Particle Size Distribution

U.S. Mesh Sieve	% Weight
+5	31.3
5-6	20.6
6-8	42.2
8-10	3.9
10-12	1.2
12-14	0.3
-14	0.5

- Grain Size

20-100 μm

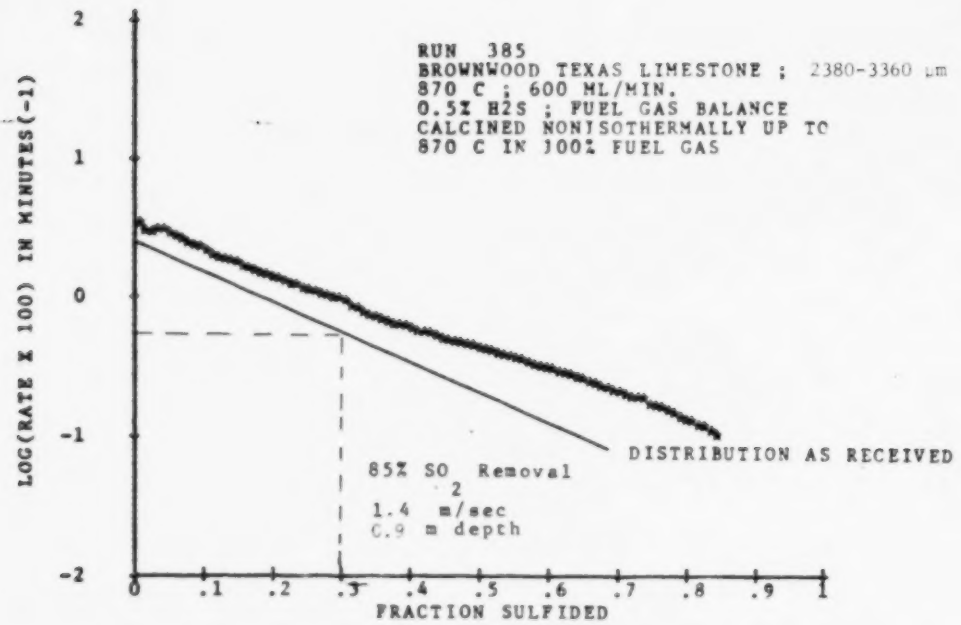

Figure 1 - Sulfidation Rate of Brownwood Limestone

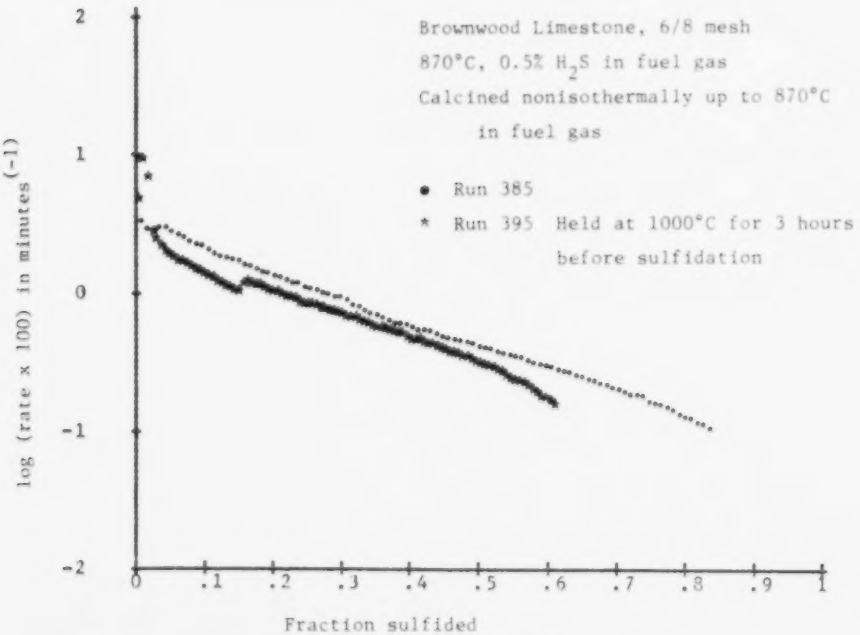
Brownwood Limestone, 6/8 mesh
870°C, 0.5% H2S in fuel gas
Calcined nonisothermally up to 870°C
in fuel gas
Run 385
Run 395 Held at 1000°C for 3 hours
before sulfidation
log (rate x 100) in minutes(-1)
Fraction sulfided

Figure 2 - Influence of Sorbent Residence Time on the Sulfidation of Brownwood Limestone

the composite rate data, 30 percent sorbent utilization is obtained. The estimated Ca/S molar feed requirement for 85 percent desulfurization is, therefore, 3/1 in a once-through process.

Effect of Sorbent Residence Time. In order to determine the effect of time at temperature on the reactivity of Brownwood stone, a large particle size fraction, 2380 to 3360 μm (6 to 8 mesh), of the sorbent was calcined and held at 1000°C for three hours in fuel gas before sulfidation. The rate curve for sulfidation, shown in Figure 2, is nearly identical to the rate curve of Brownwood limestone that was not exposed to the three-hour treatment at 1000°C. No loss of sorbent reactivity due to high temperature exposure is indicated.

Oxidation of Sulfided Brownwood Limestone. The oxidation of sulfided Brownwood limestone in air was tested on the TG apparatus as an alternative possibility for disposal of spent gasifier bed material. Since previous tests have generally shown that only a small fraction of sulfided limestone can be oxidized in air before an impenetrable sulfate shell forms, a method of activating the sorbent before it picks up sulfur was tested. The activation method used was to precalcine the sorbent at conditions that have been proved to produce a calcine with wide-mouthed pores.[23] The larger pores formed should be better able to accommodate the large sulfate ion formed when the sulfide is air oxidized to sulfate.

Air oxidation was tested on three particle size fractions of Brownwood limestone sulfided to levels of 20 to 70 percent. The sorbents were initially calcined at three conditions: 870°C in fuel gas (calcination simulating CAFB process), 900°C in 60 percent CO_2, and 850°C in 30 percent CO_2 (conditions under which calcines formed have wide-mouth pores). The results are summarized in Table 7. The calcium sulfide (CaS) fraction of 3000 μm particles that can be air oxidized at 800°C tripled as a result of sorbent pretreatment. The extent of

oxidation also increased with decreased sorbent particle size and decreased sulfidation of the sorbent. The maximum extent of oxidation that occurred, however, was about 70 percent.

Conclusions

Selection of sorbents based on their sulfidation rates is impossible because all sorbents are very active toward H_2S absorption, and organic sulfur removal by sorbents is not understood. Current sorbent screening techniques, therefore, are based on evaluating the attrition resistance of the stones and their economical availability. Trace element, regeneration, and disposal characteristics should also be considered when the information is available.

Brownwood limestone appears to be an acceptable sulfur sorbent. Limited data suggest that it is not deactivated by high-temperature (1000°C) exposure. Air oxidation of the sulfide to sulfate at 800°C does not appear to be an acceptable method of sorbent disposal. Methods for improving the possible extent of sulfide oxidation, however, were identified.

Recommendations

To develop generalized sorbent selection criteria for the CAFB process the following areas should be investigated:

- The reactivity of sorbents after exposure to the regeneration process.
- The desulfurizing mode that is not described by H_2S or SO_2 absorption. Because pilot plant data indicate that a fraction of the sulfur escapes the sorbent bed, possibly as organically based sulfur, it may be impossible to achieve 90 percent sulfur oxide (SO_x) removal by bed height, superficial velocity, and sorbent activity adjustments.

Table 7

SUMMARY OF SULFIDE OXIDATION TESTS

Particle Size, μm	% CaS Formed	% CaS Oxidized after 20 Minutes		
		No Activation, 870 C/Fuel Gas Calcination	Activation by Calcination	
			900°C/60% CO_2 Calcination	850°C/30% CO_2 Calcination
2380-3360	40	15	42	
	71	11		
420-500	40	34	56	66
	66	13		
	28			
44-74	40	51		71
	50	44	62	63
	20			

ALTERNATIVE METAL OXIDE SORBENTS

The CAFB process has been developed exclusively on the basis of using natural, calcium-based sorbents. Alternative metal oxide (MeO) sorbents may exist that could improve the regenerative performance of the CAFB process or reduce attrition losses and improve the process economics and environmental impact.

In order to investigate the potential of alternative sorbents, a three-phase screening assessment is being conducted. The first phase consists of an evaluation of sorbent thermodynamic equilibrium desulfurization and regeneration performance. The second phase considers material and energy balance limitations characteristic of the sorbents. The third phase surveys the cost and availability of the alternative sorbents and support materials. Reported here are the results of the phase I activities.

Criteria and Basis for Selecting Alternative Sorbents

A range of probable operating conditions for the CAFB process must be developed in order to provide a basis for assessing alternative Me sorbents. Table 8 lists the conditions applied to the desulfurizer-gasifier. Both the atmospheric-pressure and the pressurized CAFB concepts are evaluated. Both in-situ (as in the present calcium-based CAFB concept) and external desulfurization is considered in the thermodynamic assessment. The range of temperatures explored is based on a lower limit that may result in excessive tar formation or in limiting gasification reaction rate and an upper temperature limit that may result in sorbent sintering, deactivation, or sorbent melting. Because the gasifer can be operated over a range of air/fuel ratios from about 15 percent of stoichiometric upward to very high levels, and various methods of temperature control may be used (stack-gas recycle, steam or water injection, heat transfer surface, etc.), the fuel gas compositions may cover a very broad range. The composition presented in Table 8 is based on ERCA experimental results[5] that have been significantly broadened to provide a reasonable range for studying its impact on the

Table 8

DESULFURIZER BASIS

Fuel	Residual fuel oil
Pressures	100 kPa (1 atm) and 1500 kPa (15 atm)
Temperature Range	500°C (900°F) to 1200°C (2200°F) or sorbent melting point
Low-Heating-Value Gas Composition	1-5 mole % H_2O, 5-10% H_2, 5-12% CO, 3-8% CH_4, 1-5% C_2H_4, 5-15% CO_2, remainder N_2.
Required Thermodynamic H_2S Control Level	100 ppm

alternative sorbents. The thermodynamic level of H_2S control selected in Table 8 is based on providing sufficient kinetic driving force to satisfy the existing emission standards. Again, this number is somewhat arbitrary since the dilution of the fuel gas may vary widely, depending upon the operating conditions used. These assumptions are considered to be sufficiently accurate for the thermodynamic screening of alternative sorbents.

The following reactions are considered in the gasifier:

$$MeCO_3 \rightleftharpoons MeO + CO_2$$

$$MeO + H_2S \rightleftharpoons MeS + H_2O$$

$$MeO \xrightarrow{\text{reductants}} Me$$

Sorbent carbonate stability and MeO stability may be important sorbent limitations.

Table 9 summarizes the basis for the sorbent regenerator. Two pressure levels are selected that correspond to the atmospheric-pressure and the pressurized CAFB concepts. A temperature range of

Table 9

RE[illegible]GENERATOR BASIS

Pressures	100 kPa (1 atm) and 150 kPa (15 atm)
Temperature Range	400°C to 1400°C or sorbent melting point
Required Thermodynamic SO_2 or H_2 Level	10 mole %

100°C is applied in order to consider all potential sorbents. The sorbent melting point must not be exceeded. Thermodynamic levels of H_2S or SO_2 are selected to permit the application of relatively economical sulfur recovery technology. Three regeneration schemes that result in H_2S or SO_2 products will be considered:

$$MeS + 3/2\ O_2 \rightleftharpoons MeO + SO_2$$
$$MeS + H_2O \rightleftharpoons MeO + H_2S$$
$$MeS + CO_2 + H_2O \rightleftharpoons MeCO_3 + H_2S \quad .$$

Competing reactions may also occur in the regenerator:

$$C + O_2 \rightleftharpoons CO_2$$
$$C + H_2O \rightleftharpoons CO + H_2$$
$$MeS + ZO_2 \rightleftharpoons MeSO_4$$
$$MeO + CO_2 \rightleftharpoons MeCO_3 \quad .$$

Carbon deposited on the sorbent during gasification will be present at levels dependent upon the gasifier operating conditions. The influence of this deposited carbon is neglected for this screening study, but the effects of sulfate formation and sorbent carbonation are considered.

Alternative Sorbent Considered

Simple metal oxides (MeO_A) have been screened thermodynamically. All the MeO_A in the periodic table, ranging from lithiumoxide (Li_2O) to uranium oxide (UO_3), were initially considered, but sufficient

thermodynamic data could be found only for the following systems:[24-27] sodium oxide (Na_2O), magnesium oxide (MgO), silicon dioxide (SiO_2), calcium oxide (CaO), manganese oxide (MnO), iron oxide (FeO), ferric oxide (Fe_2O_3), (Fe_3O_4), cobalt oxide (CoO), cupric oxide (CuO), cuprite (Cu_2O), zinc oxide (ZnO), molybdenum dioxide (MoO_2), molybdenum trioxide (MoO_3), wolfram dioxide (WO_2), litharge (PbO).

Complex metal oxide forms of some of the above simple oxides such as $NaALO_2$, Na_2TiO_3, $CaAl_2O_4$, and CaV_2O_6 could be evaluated on the basis of thermodynamic data for sulfate formation,[28] but this has not been attempted.

The sorbent CaO is included in the evaluation because it may be superior to natural sorbent limestone when it is in the form of active CaO carried on an inert support such as alumina. It also provides a comparison between the well-known limestone potential and the alternative sorbent potential.

Desulfurization Performance

Four areas critical to the desulfurization performance of the alternative sorbents were considered:

- Metal oxide stability
- Metal carbonate stability
- Sorbent melting points
- Desulfurization potential.

Metal Oxide Stability

The reduction of the MeO sorbent to the base metal in the reducing atmosphere generated by the gasifier could lead to several problems: loss of desulfurization potential, the generation of low-melting point components, and so forth. The equilibrium for the reaction

$$MeO + H_2 \rightleftharpoons Me + H_2O$$

was examined for a fuel gas having a ratio of X_{H_2O}/X_{H_2} = 0.1 to 1.0 (see Table 8). Other reducing components were ignored (carbon monoxide [CO],

methane [CH_4], etc.) for this feasibility screening. If the equilibrium value of X_{H_2O}/X_{H_2O} for a given sorbent is greater than the actual fuel gas value, then we assumed that the base metal would be stable.

Of the 16 metal oxides considered five were found to be clearly unstable: CoO, CuO, CuO_2, MoO_3, and PbO. The metal oxides FeO, Fe_2O_3, Fe_3O_4, and MoO_3 are uncertain (thermodynamically), with FeO being the most stable of the iron oxide forms. The remaining sorbents are clearly stable oxides. The uncertain sorbents are considered in further screening because they may well be kinetically stable oxides.

Metal Carbonate Stability

Limited data are available for the equilibrium

$$MeCO_3 \rightleftharpoons MeO + CO_2 \quad .$$

Specific data could be found for only Na_2O, CaO, and MnO, indicating that sodium carbonate (Na_2CO_3) would be the stable sorbent form under all desulfurizer conditions, calcium carbonate ($CaCO_3$) would be stable at atmospheric pressure for temperatures lower than 700°C and at 1500 kPa (15 atm) pressure for temperatures lower than 900°C. Manganese carbonate ($MnCO_3$) would be unstable under any desulfurizer conditions.

The remaining eight sorbent materials, MgO, SiO_2, FeO, Fe_2O_3, Fe_3O_4, ZnO, MoO_2, and WO_2 are believed to be unstable as carbonates, but specific data could not be found.

Desulfurization Potential

The reaction equilibrium

$$MeO + H_2S \rightleftharpoons MeS + H_2O$$

for the remaining 11 sorbents was compared to the acceptance criteria in Table 8 (100 ppm H_2S). With water contents in the fuel gas of 1 to 5 percent, the ratio X_{H_2S}/X_{H_2O} at equilibrium must be less than 10^{-2} to 2×10^{-3}.

All of the sorbents were found to meet this criterion except MgO, Na_2CO_3, Fe_2O_3, Fe_3O_4, and SiO_2. Manganese oxide would satisfy this requirement at temperatures ranging from 400 to 800°C, WO_2 at from 400 to 500°C, MoO_2 at from 400 to 500°C, and FeO at from 400 to 650°C. The other sorbents, CaO and ZnO, satisfy the constraint over the entire temperature range considered, 400 to 1300°C.

Depending upon the desulfurizer operating conditions (air/fuel ratio, temperature control method, etc.) and the kinetics of the desulfurization reaction, the H_2S constraint applied could be relaxed to a level as high as 1000 ppm. With this relaxation Fe_2O_3 would probably become an acceptable sorbent and would broaden the temperature ranges for MnO, WO_2, MoO_2, and FeO.

Sorbent Melting Points

The melting points of the remaining six sorbents, CaO, MnO, ZnO, WO_2, FeO, and MoO_2, in the oxide, sulfide, and sulfate forms were compared to the applicable operating temperature ranges of the desulfurizer and regenerator. None of the sorbents appeared to be limited by melting except MoO_2, which melts in its oxide form at about 800°C.

Regeneration Performance

The equilibrium SO_2 generation from the reaction system (sulfide oxidation)

$$MeS + 3\ MeSO_4 \rightleftharpoons 4\ MeO + 4\ SO_2$$

was determined for $CaO/CaCO_3$, Fe_2O_3, and ZnO. The most stable oxide form of iron under oxidizing conditions is Fe_2O_3 rather than FeO. No data could be found for MnO, WO_2, or MoO_2.

In order for the sorbent to be acceptable for the sulfide oxidation scheme, the SO_2 level generated should exceed 10 mole % (Table 9). The sorbents Fe_2O_3 and ZnO will satisfy this constraint over the entire temperature range considered (400-1300°C) and at atmospheric or pressurized operation and will provide huge reaction-driving forces. The sorbent CaO will satisfy the contraint at atmospheric pressure for temperatures above 975°C and at 1500 kPa (15 atm) pressure at temperatures above 1150°C.

Alternatively, the sorbents Fe_2O_3, MnO, ZnO, WO_2, and MeO_2 may be regenerated from their sulfide form to their oxide form by reaction with steam: $MeS + H_2O \rightleftharpoons MeO + H_2S$. The H_2S criterion calls for levels greater than 10 mole % or, if we assume a pure steam reactant, the equilibrium ratio X_{H_2S}/X_{H_2O} 0.111. Only Fe_2O_3 can meet this constraint for steam regeneration at temperatures above 500°C, with a maximum H_2S level of 30 mole %.

Calcium carbonate can be regenerated by the steam/CO_2 reaction

$$CaS + H_2O + CO_2 \rightleftharpoons CaCO_3 + H_2S \quad .$$

The constraint of 10 percent H_2S can be met at neither atmospheric nor pressurized operation. A 3 mole % H_2S level can be reached at 1500 kPa (15 atm) pressure and temperatures below 700°C.

Conclusions

Six sorbents remain after thermodynamic screening: $CaO/CaCO_3$, MnO, ZnO, WO_2, FeO, and MoO_2. Table 10 summarizes the results of the screening.

The results indicate that only the $CaO/CaCO_3$ and the ZnO alternative sorbents could be used for in-situ desulfurization in a CAFB-type gasifier. The FeO-based sorbent could be used for external desulfurization at either 100 kPa (1 atm) or at 1500 kPa (15 atm) pressure. Extensive work has already been performed on FeO sorbents, indicating great potential on the basis of their highly regenerative nature.[29-31]

Table 10

SORBENT SCREENING RESULTS

	Regeneration					
	Maximum Desulfurizer Temperature °C[a]		Sulfide Oxidation Temperature Range, °C[b]		Steam or Steam/CO_2 Temperature Range, °C[c]	
Sorbent	100 kPa (1 atm) Press.	1500 kPa (15 atm) Press.	100 kPa (1 atm) Press.	1500 kPa (15 atm) Press.	100 kPa (1 atm) Press.	1500 kPa (15 atm) Press.
CaO	1300	1300	>975	>1150	No	No
$CaCO_3$	700	900	No[d]	No[d]	No	<700[g]
MnO	800	800	e	e	No	No
ZnO	1300	1300	<1300	<1300	No	No
MO_2	500	500	e	e	No	No
FeO	650	650	<1300[f]	<1300[f]	>500[f]	>500[f]
MoO_2	500	500	e	e	No	No

[a]Achieves 100 ppm SO_2 in fuel gas.
[b]Generates at least 10 mole % SO_2.
[c]Generates at least 10 mole % H_2S.
[d]The carbonate is unstable at sufficiently high temperatures.
[e]No data available.
[f]For Fe_2O_3.
[g]Generates only 3-5% H_2S.

The sorbents MnO, WO_2, and MoO_2 cannot be thermodynamically evaluated because of lack of data. On the basis of the limited data available, however, their potential does not appear great, and further assessment will be terminated.

Evaluation of the alternative sorbents $CaO/CaCO_3$, FeO (Fe_2O_3), and ZnO will continue with an assessment of material and energy balance constraints, availability, and cost feasibility.

6. ATTRITION OF FLUIDIZED-BED GASIFICATION SORBENTS

Natural materials vary in their resistance to attrition. To select sorbents one must screen them by some laboratory procedure. The objective of this study was to develop a reproducible procedure for measuring the attrition resistance of granular sorbents applicable to the CAFB.

Sorbent added to the CAFB bed first experiences thermal shock, then calcination. Jets at the grid and bubbling above the grid tumble the sorbent particles. The sorbent screening process we have developed includes all of these processes that attrite particles by thermal, chemical, and mechanical means.

The test apparatus developed is a 9.5-cm-id cell with a three-hole grid. Test temperatures are maintained by a furnace surrounding the cell. Our test procedure was to determine the gas flow required to form 8-cm-high jets in a bed of a particular sorbent. Sorbent was added to an empty bed at 900°C and fluidized for 1 hr at 815°C at the predetermined gas flow rate. Solids were sieved for particle size distribution before and after the attrition treatment.

Replicate testings of Grove, Greer, Brownwood, and Pfizer sorbents showed good repeatability between replicate tests and decisive differences in attrition tendency among different sorbents.

The apparatus and procedure developed here are not presented as a universal method but rather as a prototype. This study demonstrates that sorbents can be ranked decisively with regard to attrition tendency.

CONCLUSIONS

- An apparatus and a procedure have been demonstrated for measuring the attrition tendency of granular sorbents.

- The procedure includes the attrition mechanisms present in the grid region, the bubbling bed region, splashing in the freeboard, thermal shock, and calcination.
- The procedure for sorbent screening tested in this study discriminates decisively between the attrition tendencies of different sorbents.
- The apparatus and procedure described here are not proposed as a standard. This method serves, rather, as a prototype and demonstrates that a standard screening method can be developed.
- Brownwood limestone, while not superior in attrition resistance, is within acceptable attrition resistance limits as compared with other sorbents in these tests.

APPARATUS AND PROCEDURE

The limestone sorbents used in the CAFB are subject to attrition caused by gradual erosion or by sudden shattering. Our work has shown that several mechanisms contribute to attrition in fluidized-bed gasification.

The conditions of attrition-tendency testing must approximate conditions in the CAFB. In any event, the testing should be at fluidized-bed temperature and include the principal mechanisms of attrition. Identified causes of attrition and factors affecting attrition included in this test procedure are listed in Table 11.

The test procedure involves charging cold (room-temperature) stone to a hot (900°C) reactor and fluidizing it in such a manner that there are zones of jet action and free bubbling. A high freeboard allows ejection of particles and uncushioned falling back to the bed surface.

Apparatus

The apparatus developed for measuring attrition tendency is a cylindrical pipe 9.5 cm in diameter. The grid has three perforations so spaced that jets will be equidistant from the wall and each other. Pressure taps just above and below the grid allow the pressure drop

Table 11

POSSIBLE SOURCES OF PARTICLE ATTRITION
IN A FLUIDIZED-BED SYSTEM

Attrition Source	Application to the Test Method
1. GRID JETS. Particles are accelerated to high velocity and smash into the roof of the jet. Particles tend to shatter rather than abrade.	1. The apparatus comprises three jets, each 8 cm high.
2. BUBBLING ABOVE THE GRID JET REGIME. Bubbles cause rubbing and tumbling of particles, tendining to abrade fine chips from larger particles.	2. There is a 10-cm space above the top of the jets in which there is a vigorous bubbling.
3. THERMAL SHOCK. Sudden heating of room-temperature or colder particles to above 800°C causes severe stress and particle failure.	3. The test procedure includes pouring sorbent at 25°C into an attrition test cell preheated to 900°C, then maintaining a temperature of 815°C.
4. SPLASHING IN THE FREEBOARD. Bursting bubbles throw particles into the freeboard; falling particles collide and attrite.	4. The test cell geometry is not designed to lessen attrition from splashing.
5. TRANSFER LINES 6. CYCLONES 7. ROTARY VALVES	5, 6, 7. Particle attrition occurs in pneumatic transport and mechanical valves. While these may be part of a fluidized-bed system, they do not comprise a fluidized bed proper and are not included in the test equipment.
8. CHEMICAL REACTION. Changes in crystal lattice structure cause interfacial stress leading to fracture.	8. Not included. Sulfation is not too difficult to achieve. Sulfidation causes formation of metal eutectics and results in severe fouling and corrosion of test cell parts.
9. FLUIDIZED-BED SHAPE. A large value of the bed height to bed-diameter ratio encourages slugging and alters the extent of attrition in the bubbling zone and freeboard.	9. The height/diameter ratio is kept at less than 2 and there is no slugging.
10. BED DEPTH. Bed depth contributes an attrition force comparable to hydrostatic pressure. Local attrition rate is proportional to bed depth; average attrition rate varies with the square of bed depth.	10. Bed depth is constant at 18 cm among tests.

across the grid to be measured. The entire test cell is contained in a furnace. The system is pictured in Figure 3. The high freeboard and moderate gas velocity controlled particle carry-over; although a filter was installed in the exhaust line it captured only negligible amounts of fines.

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$$r/R = \frac{2}{2+\sqrt{3}}$$

Procedure

Our first objective was to establish gas flow conditions that would form jets 8 cm high in a bed of calcined sorbent. We filled the pipe with calcined sorbent 8 cm deep, heated the bed to 815°C and gradually increased the gas flow rate until the jets broke the surface of the bed of solids. We recorded this gas flow rate and ΔP across the grid for the following tests.

Our next objective was to measure the repeatability of extent of attrition in a bed of sorbent 18 cm deep with 8-cm-high gas jets. We heated the empty unit to 900°C and quickly poured in uncalcined sorbent at room temperature through a feed pipe to a depth of 18 cm, then capped the feed pipe. Thermal shock effects were evident: the sorbent crackled and jumped as CO_2 was liberated and the particles were heated swiftly. After capping the feed pipe we set the gas flow for jets 8 cm high, maintained a bed temperature of 815°C, and let the gas flow for one hour.

At the end of the test we turned off the furnace power and maintained a trickle flow of nitrogen through the bed to prevent intrusion of CO_2 or humid room air.

After the system had cooled we weighed and sieved the bed solids and assayed the solids for CO_2 content. It is worth noting the replicability of sieve analysis. Figure 4 shows the means and standard deviations for three replicate sievings of uniformity split

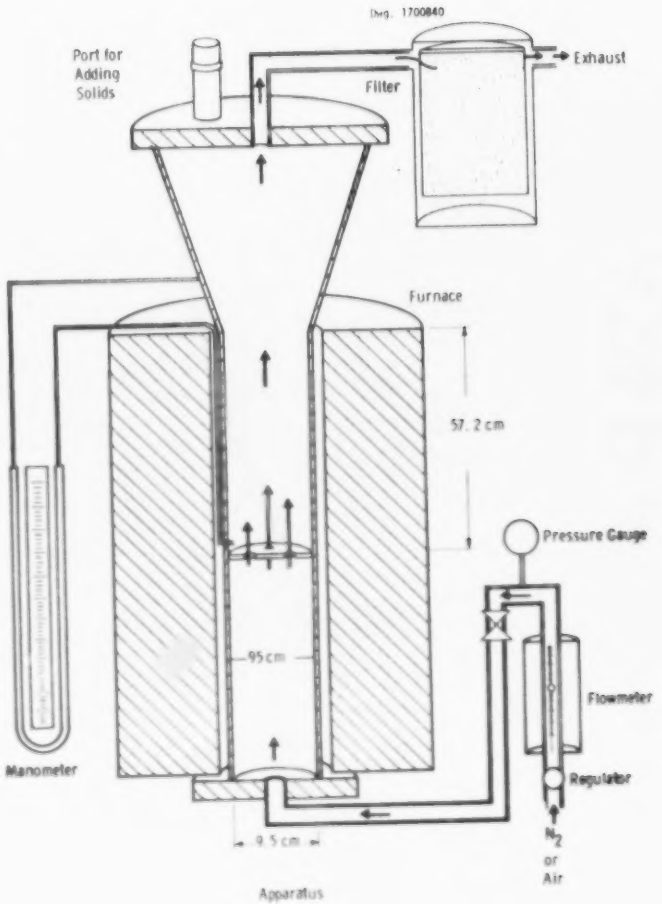


Figure 3. Sorbent Attrition Test System

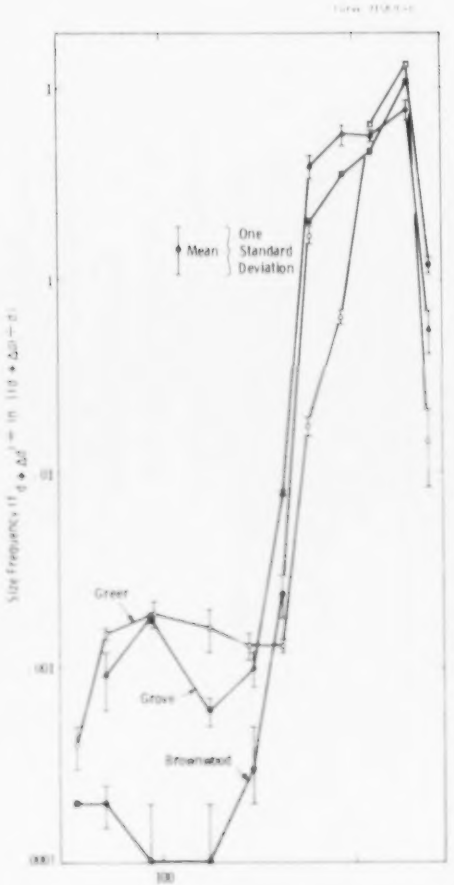


Figure 4. Mean Values and Standard Deviation of the Size Frequency Distributions for Limestone Sorbents

masses of Brownwood, Grove, and Greer sorbents. The figure is to be used in conjunction with Figure 5 in the results section to determine the significance in differences between sieve analyses. The data in Figure 4 are listed in Table 12.

RESULTS

Table 13 lists the before and after size distributions and composition data for three replicates each of three sorbents. The tests with Grove, Greer, and Brownwood limestones were run randomly to minimize time trends. Pfizer dolomite was run in three sequential tests as an afterthought. Particle size distribution data are graphed in Figure 4. Particle frequencies are shown on logarithmic ordinates to emphasize differences in small frequencies and on arithmetic ordinates to accentuate differences in the large frequencies near the mode.

The results have been interpreted in three different ways.

Table 12

MEAN VALUES AND STANDARD DEVIATIONS OF THE SIZE FREQUENCY DISTRIBUTIONS FOR LIMESTONE SORBENTS

Sieve Size		Brownwood		Grove		Greer	
Mesh	μm	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
8	2380	0.1235	0.0118	0.0568	0.0146	0.0148	0.0065
12	1810	1.1056	0.0144	0.7986	0.0948	1.3723	0.0199
16	1180	0.4812	0.0027	0.5861	0.0402	0.6657	0.0227
24	835	0.3695	0.0095	0.5970	0.0649	0.0662	0.0055
32	570	0.2094	0.0057	0.4048	0.0548	0.0177	0.0019
42	420	0.0024	0.0004	0.0079	0.0001	0.0013	0.0001
60	294	0.0003	0.0001	0.0010	0.0002	0.0013	0.0002
115	175	0.0001	0.0001	0.0006	0.0001	0.0016	0.0004
250	87	0.0001	0.0000	0.0018	0.0001	0.0019	0.0003
325	51	0.0002	0.0005	0.0009	0.0003	0.0015	0.0001
Pan	36	0.0002	--	--	--	0.0004	0.0001

Tabulated vanes are the differential frequencies (fraction at solids mass within the size range d to d + Δd) ÷ ln [d + Δd) ÷ d].

Table 13

BEFORE AND AFTER SIZE DISTRIBUTIONS AND
COMPOSITION DATA FOR TEST SORBENTS

BROWNWOOD 1

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	16	
ROTOMETER PRESSURE	15	
STONE WEIGHT BEFORE (GRAMS)	2000	43.57% CO_2
STONE WEIGHT AFTER (GRAMS)	1494.1	21.32% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL RE-HEAT CELL TO 815C FLOW N2 FOR ONE HOUR DECREPITATION

********** BEFORE **********

SUM Fi/Dpi= 7.7501
1/SUM = 0.1290
SPECIFIC SURFACE= 46.5009

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE 1.0001	f/D	f/ln
(3366)								
8	2380	2830	.346	0.042	0.0428	0.9573	0.1798	0.1237
12	1397	1810	.533	0.589	0.5891	0.3682	3.2547	1.1052
16	991	1180	.346	0.166	0.1664	0.2018	1.4105	0.4810
24	701	835	.346	0.127	0.1279	0.0739	1.5312	0.3695
32	495	570	.346	0.072	0.0725	0.0014	1.2715	0.2095
42	351	420	.346	0.000	0.0008	0.0006	0.0190	0.0023
60	246	294	.355	0.000	0.0001	0.0005	0.0034	0.0003
115	124	175	.685	0.000	0.0001	0.0004	0.0074	0.0002
250	61	87	.709	0.000	0.0002	0.0002	0.0253	0.0003
325	43	51	.349	0.000	0.0001	0.0001	0.0196	0.0003
PAN	(30)	36	.346	0.000	0.0001	0.0000	0.0278	0.0003

********** AFTER **********

SUM Fi/Dpi= 13.3974
1/SUM = 0.0746
SPECIFIC SURFACE= 80.3847

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE 0.9980	f/D	f/ln
(3366)								
8	2380	2380	.346	2.790	0.0315	0.9664	0.1325	0.0911
12	1397	1810	.533	45.820	0.5177	0.4487	2.8604	0.9714
16	991	1180	.346	15.300	0.1729	0.2758	1.4651	0.4997
24	701	835	.346	12.550	0.1418	0.1340	1.6983	0.4098
32	495	570	.346	7.220	0.0816	0.0524	1.4313	0.2358
42	351	420	.346	0.370	0.0042	0.0482	0.0995	0.0121
60	246	294	.355	0.290	0.0033	0.0450	0.1115	0.0092
115	124	175	.685	0.930	0.0105	0.0345	0.6005	0.0153
250	61	37	.709	2.100	0.0237	0.0107	2.7274	0.0335
325	43	51	.349	0.770	0.0087	0.0020	1.7060	0.0249
PAN	(30)	36	.346	0.180	0.0020	0.0000	0.5650	0.0059

BROWNWOOD 2

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	16	
ROTOMETER PRESSURE	15	
STONE WEIGHT BEFORE (GRAMS)	2000	43.57% CO_2
STONE WEIGHT AFTER (GRAMS)	1515.4	17.75% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL
RE-HEAT CELL TO 815C FLOW N2 FOR ONE HOUR DECREPITATION

********** BEFORE **********

SUM Fi/Dpi= 7.7501
1/SUM = 0.1290
SPECIFIC SURFACE= 46.5009

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					1.0001		
8	2380	2830	.346	0.042	0.0428	0.9573	0.1798	0.1237
12	1397	1810	.533	0.589	0.5891	0.3682	3.2547	1.1052
16	991	1180	.346	0.166	0.1664	0.2018	1.4105	0.4810
24	701	835	.346	0.127	0.1279	0.0739	1.5312	0.3695
32	495	570	.346	0.072	0.0725	0.0014	1.2715	0.2095
42	351	420	.346	0.000	0.0008	0.0006	0.0190	0.0023
60	246	294	.355	0.000	0.0001	0.0005	0.0034	0.0003
115	124	175	.685	0.000	0.0001	0.0004	0.0074	0.0002
250	61	87	.709	0.000	0.0002	0.0002	0.0253	0.0003
325	43	51	.349	0.000	0.0001	0.0001	0.0196	0.0003
PAN	(30)	36	.346	0.000	0.0001	0.0000	0.0278	0.0003

********** AFTER **********

SUM Fi/Dpi= 13.5917
1/SUM = 0.0735
SPECIFIC SURFACE= 81.5504

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					0.9969		
8	2380	2380	.346	3.830	0.0439	0.9530	0.1847	0.1270
12	1397	1810	.533	43.900	0.5037	0.4492	2.7830	0.9451
16	991	1180	.346	14.160	0.1625	0.2867	1.3769	0.4696
24	701	835	.346	12.630	0.1449	0.1418	1.7356	0.4189
32	495	570	.346	7.790	0.0894	0.0524	1.5682	0.2583
42	351	420	.346	0.420	0.0048	0.0476	0.1147	0.0139
60	246	294	.355	0.290	0.0033	0.0443	0.1132	0.0094
115	124	175	.685	0.900	0.0103	0.0340	0.5901	0.0151
250	61	87	.709	1.920	0.0220	0.0119	2.5323	0.0311
325	43	51	.349	0.770	0.0088	0.0031	1.7324	0.0253
PAN	(30)	36	.346	0.270	0.0031	0.0000	0.8606	0.0090

BROWNWOOD 3

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	16	
ROTOMETER PRESSURE	15	
STONE WEIGHT BEFORE (GRAMS)	2000.0	43.57% CO_2
STONE WEIGHT AFTER (GRAMS)	1658.3	28.32% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL
RE-HEAT CELL TO 815C FLOW N2 FOR ONE HOUR; FILTER ON EXHAUST
FILTER SINTERED METAL 3u 646.1gm BEFORE AND AFTER DECREPITATION

********** BEFORE **********

SUM Fi/Dpi= 7.7405
1/SUM = 0.1291
SPECIFIC SURFACE= 46.4434

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					1.0001		
3	2380	2830	.346	0.042	0.0421	0.9580	0.1760	0.1217
12	1397	1810	.533	0.590	0.5907	0.3673	3.2633	1.1082
16	991	1180	.346	0.166	0.1664	0.2009	1.4103	0.4810
24	701	835	.346	0.127	0.1273	0.0736	1.5247	0.3680
32	495	570	.346	0.072	0.0722	0.0014	1.2668	0.2087
42	351	420	.346	0.000	0.0008	0.0006	0.0190	0.0023
60	246	294	.355	0.000	0.0001	0.0005	0.0034	0.0003
115	124	175	.685	0.000	0.0001	0.0004	0.0057	0.0001
250	61	87	.709	0.000	0.0002	0.0002	0.0230	0.0003
325	43	51	.349	0.000	0.0001	0.0001	0.0196	0.0003
PAN	(30)	36	.346	0.000	0.0001	0.0000	0.0278	0.0003

********** AFTER **********

SUM Fi/Dpi= 13.9600
1/SUM = 0.0716
SPECIFIC SURFACE= 83.7601

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					0.9966		
8	2380	2380	.346	5.540	0.0511	0.9455	0.2147	0.1477
12	1397	1810	.533	58.560	0.5400	0.4055	2.9835	1.0132
16	991	1180	.346	16.090	0.1484	0.2571	1.2574	0.4288
24	701	835	.346	13.610	0.1255	0.1316	1.5031	0.3627
32	495	570	.346	8.030	0.0741	0.0575	1.2991	0.2140
42	351	420	.346	0.460	0.0042	0.0533	0.1010	0.0123
60	246	294	.355	0.330	0.0030	0.0503	0.1035	0.0086
115	124	175	.685	1.220	0.0113	0.0390	0.6429	0.0164
250	61	87	.709	2.770	0.0255	0.0135	2.9361	0.0360
325	43	51	.349	1.090	0.0101	0.0034	1.9709	0.0288
PAN	(30)	36	.346	0.370	0.0034	0.0000	0.9478	0.0099

GREER 1

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	13	
ROTOMETER PRESSURE	20	
STONE WEIGHT BEFORE (GRAMS)	2000.0	37.34% CO_2
STONE WEIGHT AFTER (GRAMS)	1412.9	10.52% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10 cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL
RE-HEAT TO 815C FLOW N2 FOR ONE HOUR DECREPITATION
WEIGHT OF FILTER ON EXHAUST DID NOT CHANGE

********** BEFORE **********

SUM Fi/Dpi= 6.7872
1/SUM = 0.1473
SPECIFIC SURFACE= 40.7235

MESH	MICRONS	MEAN	D2/D1 ln	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					1.0001		
8	2380	2830	.346	0.005	0.0051	0.9950	0.0214	0.0147
12	1397	1810	.533	0.731	0.7316	0.2634	4.0420	1.3726
16	991	1180	.346	0.230	0.2303	0.0331	1.9520	0.6657
24	701	835	.346	0.022	0.0229	0.0102	0.2743	0.0662
32	495	570	.346	0.006	0.0061	0.0041	0.1070	0.0176
42	351	420	.346	0.000	0.0005	0.0036	0.0110	0.0013
60	246	294	.355	0.000	0.0005	0.0032	0.0156	0.0013
115	124	175	.685	0.001	0.0011	0.0021	0.0629	0.0016
250	61	87	.709	0.001	0.0014	0.0007	0.1609	0.0020
325	43	51	.349	0.000	0.0005	0.0001	0.1039	0.0015
PAN	(30)	36	.346	0.000	0.0001	0.0000	0.0361	0.0004

********** AFTER **********

SUM Fi/Dpi= 7.4552
1/SUM = 0.1341
SPECIFIC SURFACE= 44.7317

MESH	MICRONS	MEAN	D2/D1 ln	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					0.9993		
8	2380	2380	.346	0.870	0.0120	0.9873	0.0506	0.0348
12	1397	1810	.533	49.240	0.6811	0.3062	3.7627	1.2778
16	991	1180	.346	18.430	0.2549	0.0513	2.1603	0.7367
24	701	835	.346	2.210	0.0306	0.0207	0.3661	0.0883
32	495	570	.346	0.710	0.0098	0.0109	0.1723	0.0284
42	351	420	.346	0.170	0.0024	0.0086	0.0560	0.0068
60	246	294	.355	0.130	0.0018	0.0068	0.0612	0.0051
115	124	175	.685	0.180	0.0025	0.0043	0.1423	0.0036
250	61	87	.709	0.190	0.0026	0.0017	0.3021	0.0037
325	43	51	.349	0.070	0.0010	0.0007	0.1898	0.0028
PAN	(30)	36	.346	0.050	0.0007	0.0000	0.1921	0.0020

GREER 2

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	13	
ROTOMETER PRESSURE	20	
STONE WEIGHT BEFORE (GRAMS)	2000.0	37.34% CO_2
STONE WEIGHT AFTER (GRAMS)	1480.6	15.10% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000cm STONE INTO CELL RE-HEAT CELL TO 815C FLOW N2 FOR ONE HOUR DECREPITATION FILTER ON EXHAUST LINE NO WEIGHT CHANGE

********** BEFORE **********

SUM Fi/Dpi= 6.7872
1/SUM = 0.1473
SPECIFIC SURFACE- 40.7235

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					1.0001		
8	2380	2830	.346	0.005	0.0051	0.9950	0.0214	0.0147
12	1397	1810	.533	0.731	0.7316	0.2634	4.0420	1.3726
16	991	1180	.346	0.230	0.2303	0.0331	1.9520	0.6657
24	701	835	.346	0.022	0.0229	0.0102	0.2743	0.0662
32	495	570	.346	0.006	0.0061	0.0041	0.1070	0.0176
42	351	420	.346	0.000	0.0005	0.0036	0.0110	0.0013
60	246	294	.355	0.000	0.0005	0.0032	0.0156	0.0013
115	124	175	.685	0.001	0.0011	0.0021	0.0629	0.0016
250	61	87	.709	0.001	0.0014	0.0007	0.1609	0.0020
325	43	51	.349	0.000	0.0005	0.0001	0.1039	0.0015
PAN	(30)	36	.346	0.000	0.0001	0.0000	0.0361	0.0004

********** AFTER **********

SUM Fi/Dpi= 6.9750
1/SUM = 0.1433
SPECIFIC SURFACE= 41.8504

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					0.9993		
8	2380	2380	.346	0.550	0.0059	0.9934	0.0246	0.0169
12	1397	1810	.533	69.030	0.7346	0.2588	4.0585	1.3782
16	991	1180	.346	21.600	0.2299	0.0289	1.9480	0.6643
24	701	835	.346	1.800	0.0192	0.0098	0.2294	0.0554
32	495	570	.346	0.360	0.0038	0.0060	0.0672	0.0111
42	351	420	.346	0.060	0.0006	0.0053	0.0152	0.0018
60	246	294	.355	0.070	0.0007	0.0046	0.0253	0.0021
115	124	175	.685	0.150	0.0016	0.0030	0.0912	0.0023
250	61	87	.709	0.150	0.0016	0.0014	0.1835	0.0023
325	43	51	.349	0.060	0.0006	0.0007	0.1252	0.0018
PAN	(30)	36	.346	0.070	0.0007	0.0000	0.2069	0.0022

GREER 3

OPERATOR NAME ; ART FELLERS
ROTOMETER SERIAL NUMBER 7311A3219A1
ROTOMETER SETTING 20
ROTOMETER PRESSURE 13
STONE WEIGHT BEFORE (GRAMS) 2000.0 37.34% CO_2
STONE WEIGHT AFTER (GRAMS) 1672.1 24.25% CO_2
STONE DEPTH (cm) 18
ATTRITION CELL USED 10cm 3 HLOE JET
ATTRITION CELL PRESURE ATM.
GAS COMPOSITION N2
COMMENT : PRE-HEAT CELL 850C LOAD 2000gm STONE INTO CELL RE-HEAT CELL 750C FLOW N2 FOR ONE HOUR DECREPITATION
FILTER ON EXHAUST LINE NO WEIGHT CHANGE

********** BEFORE **********
SUM Fi/Dpi= 6.7838
1/SUM = 0.1474
SPECIFIC SURFACE= 40.7030

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					1.0001		
8	2380	2830	.346	0.005	0.0051	0.9950	0.0180	0.0147
12	1397	1810	.533	0.731	0.7316	0.2634	4.0420	1.3726
16	991	1180	.346	0.230	0.2303	0.0331	1.9520	0.6657
24	701	835	.346	0.022	0.0229	0.0102	0.2743	0.0662
32	495	570	.346	0.006	0.0061	0.0041	0.1070	0.0176
42	351	420	.346	0.000	0.0005	0.0036	0.0110	0.0013
60	246	294	.355	0.000	0.0005	0.0032	0.0156	0.0013
115	124	175	.685	0.001	0.0011	0.0021	0.0629	0.0016
250	61	87	.709	0.001	0.0014	0.0007	0.1609	0.0020
325	43	51	.349	0.000	0.0005	0.0001	0.1039	0.0015
PAN	(30)	36	.346	0.000	0.0001	0.0000	0.0361	0.0004

********** AFTER **********
SUM Fi/Dpi= 6.7484
1/SUM = 0.1481
SPECIFIC SURFACE= 40.4906

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					0.9998		
8	2380	2830	.346	0.730	0.0147	0.9851	0.0519	0.0425
12	1397	1810	.533	36.740	0.7398	0.2453	4.0875	1.3881
16	991	1180	.346	10.560	0.2126	0.0326	1.8021	0.6146
24	701	835	.346	1.080	0.0217	0.0109	0.2605	0.0629
32	495	570	.346	0.300	0.0060	0.0048	0.1060	0.0175
42	351	420	.346	0.040	0.0008	0.0040	0.0192	0.0023
60	246	294	.355	0.040	0.0008	0.0032	0.0274	0.0023
115	124	175	.685	0.050	0.0010	0.0022	0.0575	0.0015
250	61	87	.709	0.070	0.0014	0.0008	0.1620	0.0020
325	43	51	.349	0.030	0.0006	0.0002	0.1185	0.0017
PAN	(30)	36	.346	0.010	0.0002	0.0000	0.0559	0.0006

GROVE 1

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	12	
ROTOMETER PRESSURE	11	
STONE WEIGHT BEFORE (GRAMS)	2000.0	43.97% CO_2
STONE WEIGHT AFTER (GRAMS)	1524.5	28.07% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL
RE-HEAT CELL 815C FLOW N2 FOR ONE HOUR ONLY MADE 765C
FILTER INSTALLED ON EXHAUST LINE NO WEIGHT CHANGE RECORDED
NO DECREPIATION

********** BEFORE **********

SUM Fi/Dpi= 9.3947
1/SUM = 0.1064
SPECIFIC SURFACE= 56.3685

MESH	MICRONS (3366)	MEAN	D2 ln-- D1	MASS GRAMS	***FRACTION*** DIFFER-ENTIAL	CUMULA-TIVE 1.0000	f/D	f/ln
8	2380	2830	.346	0.019	0.0197	0.9803	0.0828	0.0569
12	1397	1810	.533	0.425	0.4257	0.5546	2.3521	0.7987
16	991	1180	.346	0.202	0.2028	0.3518	1.7187	0.5862
24	701	835	.346	0.206	0.2066	0.1452	2.4744	0.5971
32	495	570	.346	0.140	0.1401	0.0051	2.4580	0.4049
42	351	420	.346	0.002	0.0027	0.0024	0.0643	0.0078
60	246	294	.355	0.000	0.0004	0.0020	0.0122	0.0010
115	124	175	.685	0.000	0.0004	0.0016	0.0206	0.0005
250	61	87	.709	0.001	0.0013	0.0003	0.1529	0.0019
325	43	51	.349	0.000	0.0003	0.0000	0.0588	0.0009

********** AFTER **********

SUM Fi/Dpi= 8.9431
1/SUM = 0.1118
SPECIFIC SURFACE= 53.6587

MESH	MICRONS (3366)	MEAN	D2 ln-- D1	MASS GRAMS	***FRACTION*** DIFFER-ENTIAL	CUMULA-TIVE 0.9999	f/D	f/ln
8	2380	2380	.346	2.370	0.0245	0.9754	0.1031	0.0709
12	1397	1810	.533	43.890	0.4543	0.5210	2.5102	0.8524
16	991	1180	.346	20.680	0.2141	0.3069	1.8142	0.6187
24	701	835	.346	13.010	0.1864	0.1205	2.2328	0.5388
32	495	570	.346	11.070	0.1146	0.0059	2.0105	0.3312
42	351	420	.346	0.320	0.0033	0.0026	0.0789	0.0096
60	246	294	.355	0.090	0.0009	0.0017	0.0317	0.0026
115	124	175	.685	0.090	0.0009	0.0007	0.0532	0.0014
250	61	87	.709	0.050	0.0005	0.0002	0.0595	0.0007
325	43	51	.349	0.010	0.0001	0.0001	0.0203	0.0003
PAN	(30)	36	.346	0.010	0.0001	0.0000	0.0288	0.0003

GROVE 2

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	/311A3219A1	
ROTOMETER SETTING	12	
ROTOMETER PRESSURE	11	
STONE WEIGHT BEFORE (GRAMS)	2000.0	43.97% CO_2
STONE WEIGHT AFTER (GRAMS)	1533.8	25.84% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL RE-HEAT CELL TO 815C FLOW N 2 FOR ONE HOUR NO DECREPITATION FILTER ON EXHAUST LINE NO CHANGE

********** BEFORE **********

SUM Fi/Dpi= 9.3316
1/SUM = 0.1065
SPECIFIC SURFACE= 56.2896

MESH	MICRONS	MEAN	D2 ln-- D1	MASS GRAMS	***FRACTION*** DIFFER-ENTIAL	CUMULA-TIVE	f/D	f/ln
	(3366)					1.0000		
8	2380	2830	.346	0.019	0.0197	0.9803	0.0696	0.0569
12	1397	1810	.533	0.425	0.4257	0.5546	2.3521	0.7987
16	991	1180	.346	0.202	0.2028	0.3518	1.7187	0.5862
24	701	835	.346	0.206	0.2066	0.1452	2.4744	0.5971
32	495	570	.346	0.140	0.1401	0.0051	2.4580	0.4049
42	351	420	.346	0.002	0.0027	0.0024	0.0643	0.0078
60	246	294	.355	0.000	0.0004	0.0020	0.0122	0.0010
115	124	175	.685	0.000	0.0004	0.0016	0.0206	0.0005
250	61	87	.709	0.001	0.0013	0.0003	0.1529	0.0019
325	43	51	.349	0.000	0.0003	0.0000	0.0588	0.0009

********** AFTER **********

SUM Fi/Dpi= 8.7928
1/SUM = 0.1137
SPECIFIC SURFACE= 52.7570

MESH	MICRONS	MEAN	D2 ln-- D1	MASS GRAMS	***FRACTION*** DIFFER-ENTIAL	CUMULA-TIVE	f/D	f/ln
	(3366)					0.9999		
8	2830	2830	.346	2.810	0.0299	0.9700	0.1056	0.0863
12	1397	1810	.533	44.070	0.4685	0.5015	2.5883	0.8790
16	991	1180	.346	19.570	0.2080	0.2935	1.7630	0.6013
24	701	835	.346	17.120	0.1820	0.1115	2.1795	0.5260
32	495	570	.346	9.830	0.1050	0.0065	1.8426	0.3035
42	351	420	.346	0.320	0.0034	0.0031	0.0810	0.0098
60	246	294	.355	0.110	0.0012	0.0019	0.0398	0.0033
115	124	175	.685	0.100	0.0011	0.0009	0.0607	0.0016
250	61	87	.709	0.050	0.0005	0.0003	0.0611	0.0007
325	43	51	.349	0.020	0.0002	0.0001	0.0417	0.0006
PAN	(30)	36	.346	0.010	0.0001	0.0000	0.0295	0.0003

GROVE 3

OPERATOR NAME ;	ART FELLERS	
ROTOMETER SERIAL NUMBER	7311A3219A1	
ROTOMETER SETTING	12	
ROTOMETER PRESSURE	11	
STONE WEIGHT BEFORE (GRAMS)	2000.0	43.97% CO_2
STONE WEIGHT AFTER (GRAMS)	1618.4	30.28% CO_2
STONE DEPTH (cm)	18	
ATTRITION CELL USED	10cm 3 HOLE JET	
ATTRITION CELL PRESURE	ATM.	
GAS COMPOSITION	N2	

COMMENT : PRE-HEAT CELL 900C LOAD 2000gm STONE INTO CELL RE-HEAT CELL TO 815C FLOW N2 FOR ONE HOUR NO DECREPITATION FILTER ON EXH

********** BEFORE **********

SUM Fi/Dpi= 9.3947
1/SUM = 0.1064
SPECIFIC SURFACE= 56.3685

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					1.0000		
8	2380	2830	.346	0.019	0.0197	0.9803	0.0828	0.0569
12	1397	1810	.533	0.425	0.4257	0.5546	2.3521	0.7987
16	991	1180	.346	0.202	0.2028	0.3518	1.7187	0.5862
24	701	835	.346	0.206	0.2066	0.1452	2.4744	0.5971
32	495	570	.346	0.140	0.1401	0.0051	2.4580	0.4049
42	351	420	.346	0.002	0.0027	0.0024	0.0643	0.0078
60	246	294	.355	0.000	0.0004	0.0020	0.0122	0.0010
115	124	175	.685	0.000	0.0004	0.0016	0.0206	0.0005
250	61	87	.709	0.001	0.0013	0.0003	0.1529	0.0019
325	43	51	.349	0.000	0.0003	0.0000	0.0588	0.0009

********** AFTER **********

SUM Fi/Dpi= 8.9284
1/SUM = 0.1120
SPECIFIC SURFACE= 53.5704

MESH	MICRONS	MEAN	D2/D1 ln--	MASS GRAMS	***FRACTION*** DIFFERENTIAL	CUMULATIVE	f/D	f/ln
	(3366)					0.9998		
8	2380	2380	.346	1.510	0.0255	0.9744	0.1070	0.0736
12	1397	1810	.533	22.450	0.3785	0.5959	2.0913	0.7102
16	991	1180	.346	19.830	0.3343	0.2615	2.8334	0.9663
24	701	835	.346	9.340	0.1575	0.1040	1.8860	0.4551
32	495	570	.346	5.860	0.0988	0.0052	1.7334	0.2856
42	351	420	.346	0.170	0.0029	0.0024	0.0682	0.0083
60	246	294	.355	0.040	0.0007	0.0017	0.0229	0.0019
115	124	175	.685	0.050	0.0008	0.0008	0.0482	0.0012
250	61	87	.709	0.030	0.0005	0.0003	0.0581	0.0007
325	43	51	.349	0.010	0.0002	0.0002	0.0331	0.0005
PAN	(30)	36	.346	0.010	0.0002	0.0000	0.0468	0.0005

PFIZER 1

ATTRITION WITH 3-HOLE JET IN 10-CM B&D
UNCALCINED -18+32 PFIZER SORBENT

OPERATOR NAME: ART FELLERS
ROTOMETER SETTING: 20.
ROTOMETER PRESSURE: 13.
STONE WEIGHT BEFORE (GRAMS): 2000.0
STONE WEIGHT AFTER (GRAMS): 777.2
STONE DEPTH (CM): 18.0
ATTRITION CALL USED: 10 CM 3HOLE JET
ATTRITION CALL PRESSURE: ATM
GAS COMPOSITION: N2
COMMENT: REPESENTATIVE SAMPLE BEFORE AND AFTER
PREHEAT CELL 860C POUR 2000G STONE IN
REHEAT CELL 765C THEN FLOW N2 1HR
DECREPIATION

***** BEFORE

MESH	MICRONS	MEAN	LN(D2/D1)	MASS GRAMS	****FRACTION**** DIFFER-ENTIAL	CUMULA-TIVE	F/D	F/LN
	(3337)					1.0000		
8	2360	2806	.346	.000	.0000	1.0000	.0000	.0001
12	1397	1815	.524	11.920	.1763	.8237	.9712	.3362
16	991	1176	.343	27.430	.4056	.4181	3.4494	1.1814
24	701	833	.346	24.380	.3605	.0575	4.3283	1.0414
32	495	589	.348	3.870	.0572	.0003	.9717	.1645
42	351	416	.344	.020	.0003	.0000	.0071	.0009
60	246	293	.355	.000	.0000	.0000	.0000	.0001
115	124	174	.685	.000	.0000	.0000	.0000	.0001
250	61	86	.709	.000	.0000	.0000	.0000	.0001
325	43	51	.350	.000	.0000	.0000	.0000	.0001
PAN	30	35	.360	.000	.0000	.0000	.0000	.0001

SURFACE MEAN EQUIVALENT PARTICLE SIZE, CM = .1028
SPECIFIC SURFACE, CM**(-1) = 58.3661

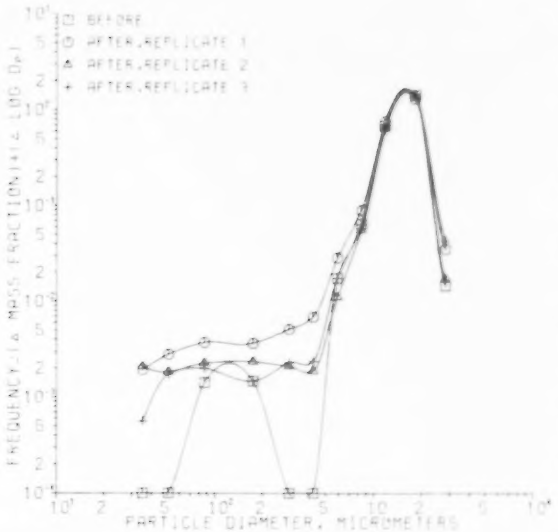
***** AFTER

MESH	MICRONS	MEAN	LN(D2/D1)	MASS GRAMS	****FRACTION**** DIFFER-ENTIAL	CUMULA-TIVE	F/D	F/LN
	(3337)					1.0000		
8	2360	2806	.346	.000	.0000	1.0000	.0000	.0001
12	1397	1815	.524	2.930	.0625	.9375	.3444	.1192
16	991	1176	.343	18.970	.4047	.5328	3.4416	1.1787
24	701	833	.346	16.570	.3535	.1792	4.2441	1.0212
32	495	589	.348	4.110	.0877	.0915	1.4888	.2520
42	351	416	.344	.430	.0092	.0824	.2205	.0267
60	246	293	.355	.400	.0085	.0738	.2913	.0240
115	124	174	.685	.980	.0209	.0529	1.2017	.0305
250	61	86	.709	1.490	.0318	.0211	3.6965	.0448
325	43	51	.350	.670	.0143	.0068	2.8029	.0409
PAN	30	35	.360	.320	.0068	.0000	1.9507	.0190

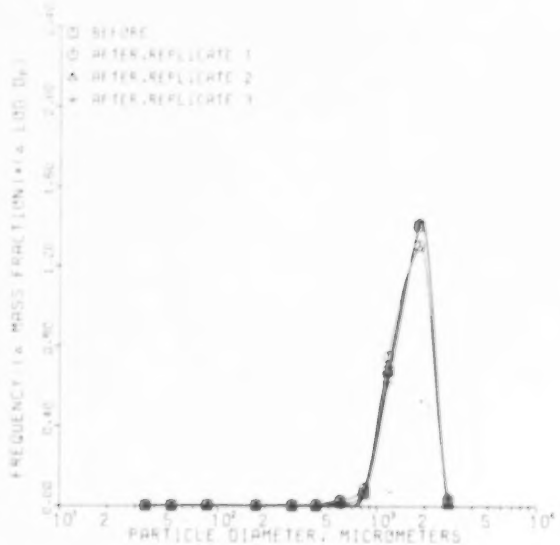
SURFACE MEAN EQUIVALENT PARTICLE SIZE, CM = .0508
SPECIFIC SURFACE, CM**(-1) = 118.0950

Figure 5

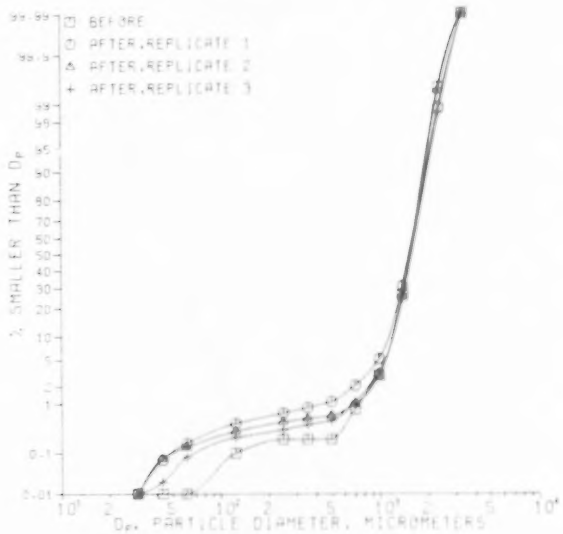
PARTICLE SIZE FREQUENCY CURVES FOR ATTRITION
SCREENING TREATMENT OF SORBENTS



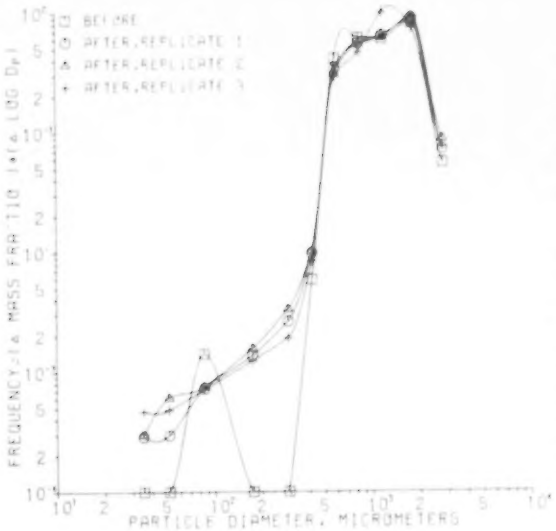
Particle-Size Distribution of Greer Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Logarithmic Scale



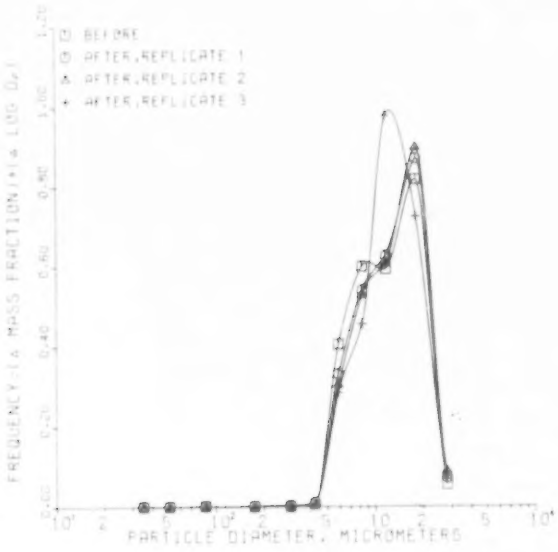
Particle-Size Distribution of Greer Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Linear Scale



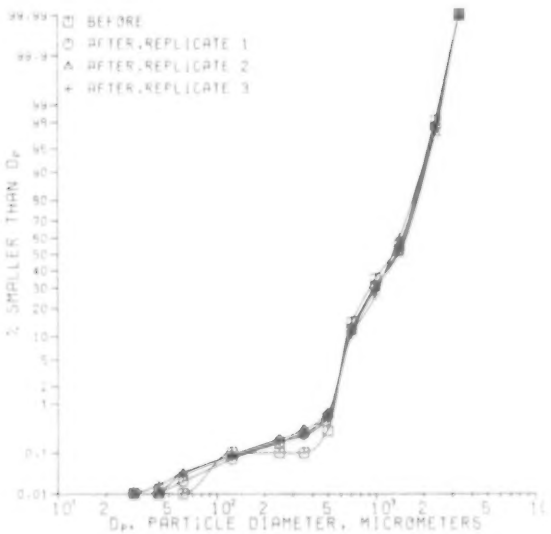
Particle-Size Distribution of Greer Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Probability Scale



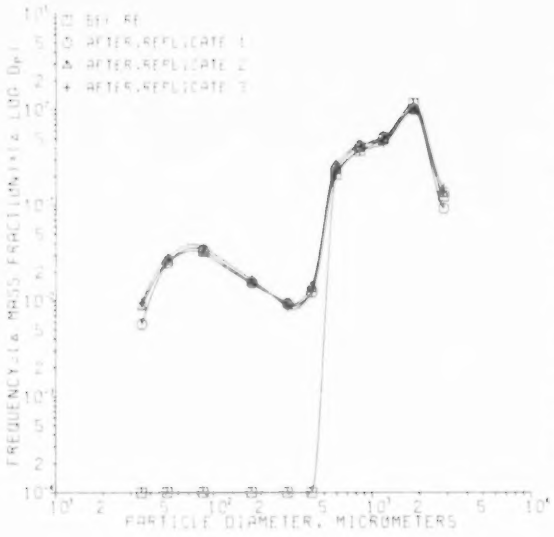
Particle-Size Distribution of Grove Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Logarithmic Scale



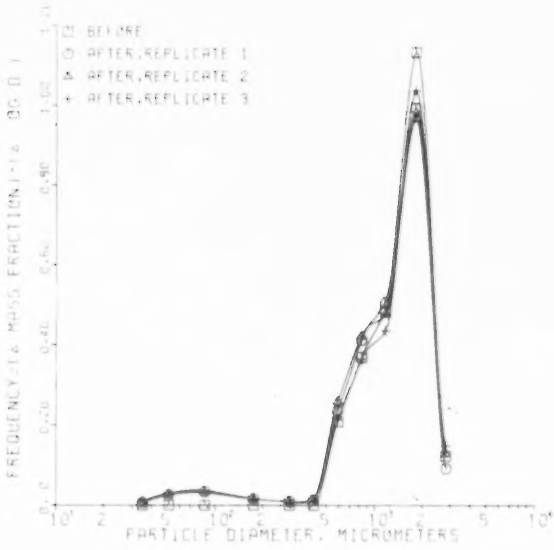
Particle-Size Distribution of Grove Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Linear Scale



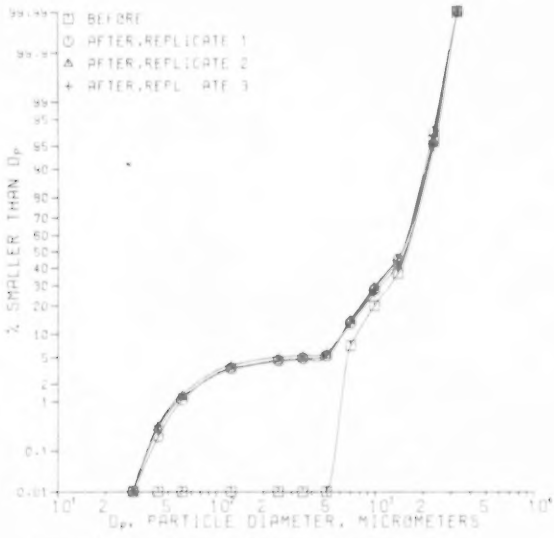
Particle-Size Distribution of Grove Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Probability Scale



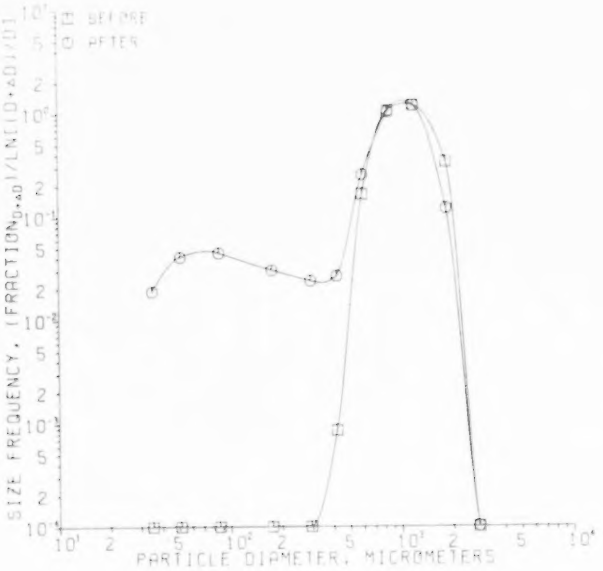
Particle-Size Distribution of Brownwood Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Logarithmic Scale



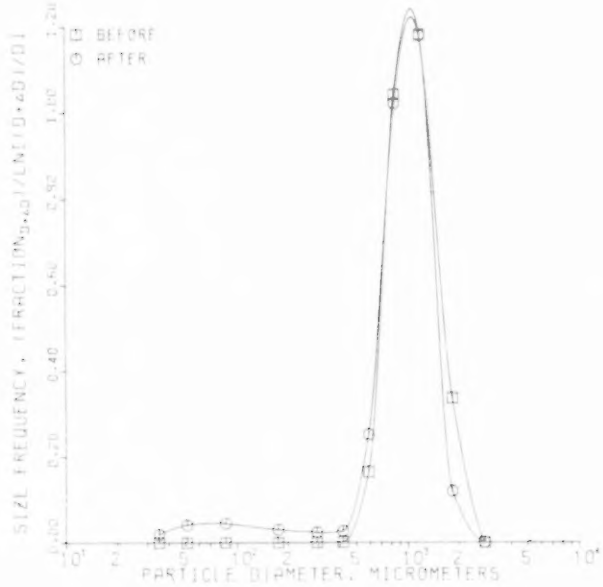
Particle-Size Distribution of Brownwood Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Linear Scale



Particle-Size Distribution of Brownwood Limestone. Attrition Testing in 10-cm Bed with 3-Hole Grid. Ordinate is Probability Scale



Attrition with 3-Hole Jet in 10-cm
B Uncalcined -18 +32 Pfizer Sorbent.
Ordinate is Logarithmic Scale



Attrition with 3-Hole Jet in 10-cm
B Uncalcined -18 +32 Pfizer Sorbent.
Ordinate is Linear Scale

First, the increases in specific surface, listed in Table 14, are compared by completely randomized analysis of variance. Testing at the 5-percent level shows significant differences among all three means and between the Greer and Grove means.

Second, in interpreting these data, the increase in mass fraction of particles smaller than 495 μm are listed and analyzed in Table 15. Again, testing at the 5-percent level shows significant differences among all three means and between the Greer and Grove means.

The third approach is comparing effects of both sieve size and sorbent on frequency. We cannot compare all sieves because the frequencies are not independent but choose those sieves smaller than 701 μm.

Table 14

SPECIFIC SURFACE INCREASE DATA AND ANALYSIS OF VARIANCE OF DIFFERENCES

Replicate	Sorbent								
	1. Brownwood			2. Greer			3. Grove		
	Before	After	Diff.	Before	After	Diff.	Before	After	Diff.
1	46.50	80.38	33.88	40.72	44.73	4.01	56.37	53.66	-2.71
2	46.50	81.55	35.05	40.72	41.85	1.13	56.37	52.76	-3.53
3	46.44	83.76	37.32	40.70	40.49	0.21	56.37	53.57	-2.79

Analysis of Variance on Differences:

Source	Sum Sq	DF	Mean Sq	F-Ratio
Column Means	2620.6	2	1310.3	442.6
Within Cols.	17.8	6	2.96	
Total	2638.4	8		

Individual DF Test on Greer & Grove Effects:

$$F = \frac{4.01 + 1.13 - 0.21 + 2.71 + 3.53 + 2.79}{3(1^2 + (-1)^2)2.96} = 10.97 \text{ with } 1 \text{ \& } 8 \text{ df.}$$

Table 15

INCREASES IN SORBENT FRACTIONS <495 μm AND ANALYSIS OF VARIANCE OF DIFFERENCES

Replicate	Sorbent								
	1. Brownwood			2. Greer			3. Grove		
	Before	After	Diff.	Before	After	Diff.	Before	After	Diff.
1	0.0014	0.0524	0.051	0.0041	0.0109	0.0068	0.0051	0.0059	0.0008
2	0.0014	0.0524	0.051	0.0041	0.0060	0.0019	0.0051	0.0065	0.0014
3	0.0014	0.0575	0.056	0.0041	0.0068	0.0007	0.0051	0.0052	0.0001

Analysis of Variance on Diferences:

Source	Sum Squares	DF	Mean Square	F-Ratio
Column Means	0.0000384	2	0.00258	402.56259
Within Columns	0.00519	6	0.00000640	
Total	0.00519	8		

Individual DF Test on Greer and Grove Effects:

$$F = \frac{0.0068 + 0.0019 + 0.0007 - 0.0008 - 0.0014 - 0.0001}{3(1^2 + (-1)^2)(0.00000640)} = 184 \text{ with 1 \& 8 df}$$

Table 16 lists frequency-increase data of a two-way analysis of variance. The column (sorbent) means give rise to an F-ratio of 3.56 which signals a significant difference (tabulated F = 3.2 with 2 and 42 df) at the 5-percent level.

Inspection of any of three different aspects of these data show that there are indeed significant differences in degree of attrition among the sorbents tested.

Table 16

FREQUENCY INCREASE DATA FOR SIEVES SMALLER THAN 701 μm AND TWO-WAY (randomized block) ANALYSIS OF VARIANCE

Sieve Size Range, μm	Values of Frequency Increase		
	Sorbent		
	1. Brownwood	2. Greer	3. Grove
495-701	0.0213 0.0488 0.0053	0.0001 0.0065 0.0108	0.0737 0.1014 0.1193
351-495	0.0098 0.0116 0.0100	0.0010 0.0005 0.0055	0.0018 0.0020 0.0005
246-351	0.0089 0.0091 0.0083	0.0010 0.0008 0.0038	0.0016 0.0023 0.0009
124-246	0.0151 0.0149 0.0163	0.0001 0.0005 0.0020	0.0009 0.0011 0.0017
61-124	0.0332 0.0308 0.0357	0.0000 0.0003 0.0017	0.0008 0.0008 0.0012
43-61	0.0246 0.0250 0.0285	0.0002 0.0003 0.0013	0.0006 0.0003 0.0004
<43	0.0056 0.0087 0.0096	0.0002 0.0018 0.0016	0.0003 0.0003 0.0005

Table 16 evidences some consistent negative frequency changes with the Greer and Grove sorbents. These values are small and probably attributable to random chance as loss by attrition rather than to gain by attrition. The Grove sorbent curve (Figure 5) consistently shows a net loss of particle mass in the 400 to 800 μm size range. This size appears to attrite preferentially, perhaps because of grain structure.

DISCUSSION

Our purpose here has been to develop a screening test that embodies the attrition mechanisms active in the CAFB.

The procedure tested involves the principal attrition sources. There is probably a "reasonable" range of effects for each attrition cause. We have attempted to duplicate this, but the balance is imperfect. For example, the sources of attrition in a given system may be almost entirely grid jet effects; in the test described here, thermal shock is a prime contributor to attrition.

It is premature to specify a standard piece of equipment for attrition testing. It is practicable, however, to specify a procedure, describe the apparatus, and recommend a "good enough" reference or standard sorbent against which others may be compared.

For attrition testing of candidate sorbents for CAFB we suggest use of an attrition test cell congruent with that described here and the same test procedure. Either Grove 1359 limestone or Greer limestone is suggested as an adequate reference because they are comparable in attrition resistance, and both are adequate in attrition and sorption performance.

7. PARTICULATE CONTROL

The control of particulate emissions from the CAFB is a critical area since the process operability and environmental acceptability depend on the control success. Particulate control requirements and control options are discussed on the basis of parametric projections.

CONTROL REQUIREMENTS

The CAFB particulate control requirements have been considered parametrically for two cases: gasification of liquid fuels (residual fuel oils and bitumen) and gasification of lignite. The gasifier is the major source of particulate emissions, with the regenerator, the spent sorbent processing system, the sulfur recovery system, and the sorbent (and lignite) handling systems of secondary importance.

The control of particulate from the gasifier must meet three general requirements: minimization of coarse sorbent particle losses; protection of the fuel gas piping, the burner, and the boiler from erosion and deposits; and environmental particulate emission standards of 4.3×10^{-5} kg/GJ (0.1 lb/10^6 Btu). In general, particulate control will be required before and after the boiler in order to meet these requirements.

The following two figures represent the particulate control efficiency requirements before and after the boiler as a function of the sorbent elutriation rate for commercial CAFB installations. The sorbent elutriation rate is expressed as a fraction of the fresh sorbent feed rate.

Figure 6 considers two fuels, residual fuel oil and bitumen with 2.6 wt % sulfur and 3.75 wt % sulfur, respectively. Two calcium-to-sulfur ratios are shown - 0.5 and 1.0 - based on the expected range of gasifier performance from pilot plant experience.

Figure 7 considers lignite having a 15 wt % ash content and 3.6 wt % sulfur content. The fraction of the lignite ash elutriated from the gasifier is a parameter in the figure having three values - 0.25, 0.5, and 1.0.

The control requirements before the boiler are difficult to quantify, but we expect that if control before the boiler is utilized the control device should be of as high an efficiency as can be tolerated in terms of the fuel gas pressure drop and system operability, since the capital investment will probably not be too sensitive to collection efficiency for a given control technique. A very high elutriation rate (>100% of the fresh sorbent feed rate) probably would result from a high carry-over of coarse material which should be captured to the greatest extent possible. A small elutriation rate (<10% of the fresh sorbent feed rate) probably would result from attrition and carry-over of fine material which should be removed from the system (for spent sorbent processing) rather than recycled to the gasifier or regenerator.

The lignite ash should be removed from the system without recycle to the greatest extent possible in order to avoid ash agglomeration problems and high ash carry-over rates. Ash separation from coarse sorbent particles may be possible, depending on the nature of the ash (size, density, shape). Multiple stages of particulate control may be required.

CONTROL OPTIONS

The control technology available for the CAFB is as follows: cyclones, granular-bed filters, conventional filter systems, scrubbing systems, electrostatic precipitators. Any of these could be used after the boiler, while only the cyclones or granular-bed filters will be considered for the hot low-heating-value gas cleaning before the boiler.

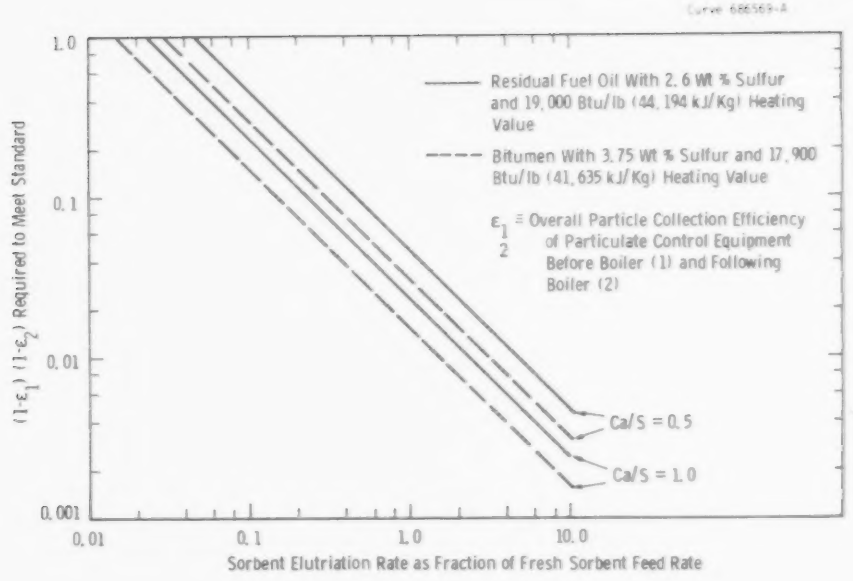

Curve 686569-A
1.0
0.1
0.01
0.001
0.01
0.1
1.0
10.0
$(1-\epsilon_1)(1-\epsilon_2)$ Required to Meet Standard
Sorbent Elutriation Rate as Fraction of Fresh Sorbent Feed Rate
Residual Fuel Oil With 2.6 Wt % Sulfur and 19,000 Btu/lb (44,194 kJ/Kg) Heating Value
Bitumen With 3.75 Wt % Sulfur and 17,900 Btu/lb (41,635 kJ/Kg) Heating Value
$\epsilon_{1\ 2}$ ≡ Overall Particle Collection Efficiency of Particulate Control Equipment Before Boiler (1) and Following Boiler (2)
Ca/S = 0.5
Ca/S = 1.0

Figure 6. Oil-Fueled CAFB Particulate Control Requirements

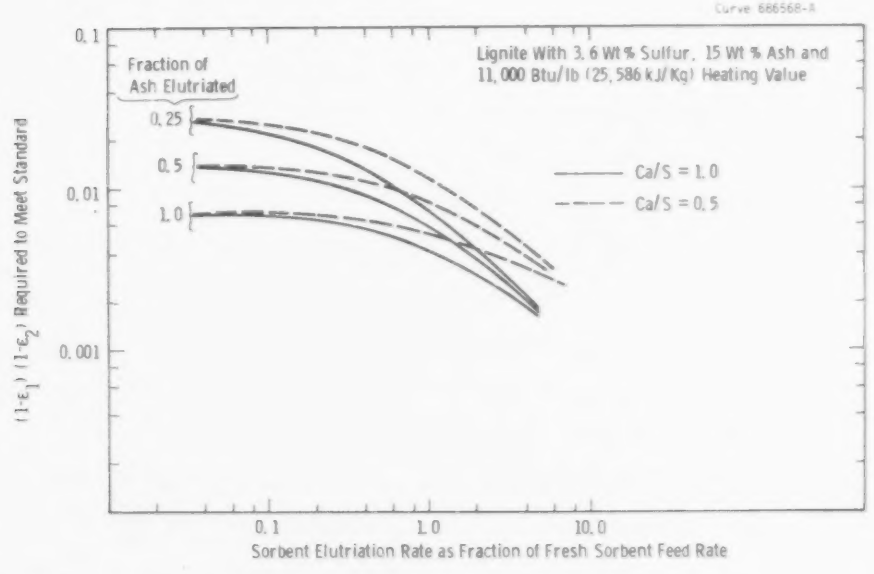


Figure 7. Coal-Fueled CAFB Particulate Control Requirements

Because the nature of the low-heating-value gas is to form deposits and cause plugging and because of the possible need for sorbent recycle from the collection device, we recommend that conventional cyclones be used before the boiler. High efficiency from these cyclones can not be expected because of deposit formation. We have selected an upper limit of 90% overall efficiency for sorbent material as a basis. As in Figure 6 for the gasification of residual fuel oil or bitumen and if we assume a cyclone collection efficiency of 90 percent, no particulate control would be required after the boiler if less than 15 percent of the fresh sorbent rate were elutriated from the gasifier in the case of bitumen and 25 percent in the case of residual fuel oil.

As in Figure 7 for the gasification of lignite, we expect that either multiple cyclones will be required before the boiler or some form of particulate control will be required after the boiler under all reasonable conditions of elutriation. Depending on the nature of the lignite ash, either a conventional cyclone or an electrostatic precipitator would be recommended after the boiler.

ASSESSMENT

Table 17 summarizes recommendations and limitations of the recommendations. On the basis of pilot plant elutriation results, we expect that liquid fuel gasification will require particulate control by conventional cyclones before and after the boiler. We project lignite gasification to require a conventional cyclone before the boiler and an electrostatic precipitator for final control. These conclusions will be valid over a broad range of performance.

Additional alternatives that could be applied to reduce particle elutriation from the gasifier are: reduced fluidization velocity, shallow bed operation, increased freeboard height or baffles in the freeboard, improved distributor plate design, limited recycle of fines from the particulate control system to the gasifier, improved sorbent feeding

Table 17

CAFB PARTICULATE CONTROL REQUIREMENTS

Cases	Residual Fuel Oil	Bitumen	Lignite, % Ash Elutriated	
			25	100
No Control Required[a]	<2.5	<1.5	Always required	Always required
Cyclone before Boiler[b]	>2.5 <25	>1.5 <15	Not sufficient	Not sufficient
Series Cyclones before Boiler or before and after Boiler[c]	>25 <250	>15 <150	>0 <65	Not sufficient
Cyclone before Boiler and ESP after Boiler[d]	>250	>150	>65	>0

[a]Assumes gas lines, burners, boiler unaffected by erosion, deposits.

[b]Maximum overall cyclone efficiency 90%; dependent upon size distribution, deposit formation, pressure drop limitations.

[c]Assumes maximum efficiency of 2 cyclones in series of 99%.

[d]Assumes maximum cyclone efficiency of 90% and electrostatic precipitator (ESP) efficiency of 99%. Very sensitive to lignite ash characteristics.

method to avoid fast heating and calcination, sorbent selection based on attrition resistance, sorbent preparation by sizing or prehardening, and lignite sizing and washing.

There are no development requirements for cyclone or electrostatic precipitator particulate control except to demonstrate long-term reliability and performance of the cyclone with hot, low-heating-value gas particulate control. The alternatives listed to reduce particle elutriation would require design evaluation and/or development work before any of them could be implemented.

Data gaps exist in the areas of sorbent attrition and elutriation behavior, lignite ash characteristics and elutriation behavior; commercial cyclone performance in the CAFB low-heating-value gas environment; and erosion and deposit effects in the fuel gas line, burner, and boiler. The availability of such data would permit improved projections of particulate control requirements but would probably not change the general conclusions developed.

8. ASSESSMENT

PROCESS ECONOMICS

There are many options to consider in assessing CAFB Process Economics:

New vs retrofit
Once-through vs regenerable
CAFB vs stack scrubbing
CAFB vs hydrodesulfurization
CAFB vs gasification
CAFB vs Flexicoking (SM)
CAFB vs coal liquefaction

Some of these choices can be resolved relatively easily. It is unlikely, for example, that a new CAFB-fueled boiler could be justified. New boilers on feedstocks appropriate for CAFB should probably utilize fluidized-bed combustion (FBC). Also, the federal policy of coal utilization for new boilers dictates against CAFB, and, in general, the feedstock problems discussed in Section 4 of this report indicate little likelihood of fueling new boilers with residue from oil refining or from synfuel production. Further, the 1975 CAFB[3] assessment indicates that both once-through and regenerative stack-gas cleaning processes are lower in investment and operating cost than a CAFB unit for 50, 200, and 500 MW power boilers, so these stack-scrubbing options are likely to be used to meet the requirements placed on new units by the EPA New Source Performance Standards (NSPS).[32] The economic assessment prepared by GCA Corporation for EPA in 1979 reaches the same conclusion in its comparison of 250 MW regenerable systems.[33] The GCA report indicates $260/kW investment and $5.90/bbl of fuel oil feed operating cost for CAFB vs $92/kW and $2.63/bbl for regenerable MgO flue gas desulfurization. Thus, new regenerable CAFB is too costly.

The GCA report also provides a basis for an ecomonic assessment of once-through vs regenerable options. The once-through CAFB system costs, if we assume dry sulfation of the sulfided limestone, are $188/kW and $4.38/bbl, which is less than 75 percent of the regenerable CAFB system cost. This once-through CAFB system, however, is still substantially more costly than the regenerable flue gas desulfurization system, so a once-through system is also too costly for new CAFB installations. It does appear that once-through CAFB has significantly better economics than regenerable CAFB and should be the process to use in any comparison with options such as hydrodesulfurization or Flexicoking. (SM) CAFB does provide the potential to use a high heavy-metal-content residuum that cannot be burned directly in conventional boilers because of boiler tube corrosion/deposition problems. In such a case the flue gas desulfurization option would not apply, and some fuel processing system would need to be used.

The GCA report also addresses Flexicoking[15] and hydrodesulfurization (LC-Fining)[34] economics relative to once-through CAFB.

	Once-through CAFB	Flexicoking	LC Fining
Investment, $/kW	188	107	95
Operation, $/bbl	4.38	3.45	3.84

In its analysis of these results, GCA concludes that "in order to operate the CAFB on a competitive basis . . . high sulfur, high metals crudes must be $2 to $3 per barrel cheaper" and "at present this per barrel differential requirement is roughly twice the market situation." As discussed in Section 4, the tight crude oil supply today, the projection that this situation will be the norm for the 1980s, the increasing need for hydrogen[35] in processing heavy crudes, the developing needs for transportation fuels in Third World Nations, and a reduction in U.S. oil imports as a matter of national security all indicate that the $2 to 3/bbl price differential is unlikely.

To supplement the GCA economic assessment we have prepared an assessment of CAFB relative to some "synfuels" options such as oil and coal gasification and coal liquefaction. The results of this assessment reinforce the conclusion that refiners will utilize vacuum bottoms for hydrogen production before using coal, so that every oil fraction will be used before they resort to coal. In order to minimize confusion (the GCA assessment was for a 200 MW unit in 1980; the Westinghouse assessment was for a 200 MW unit in 1977) we have normalized our cost data to the $5.90/bbl operating cost of GCA's regenerable CAFB and Resox™ System. Table 18 indicates relative costs to operate each of the systems.

It is obvious that:

- Vacuum bottoms will be used as a hydrogen source in preference to coal (O_2 gasification of resid vs coal).
- Vacuum bottoms will be used as a fuel gas source in preference to coal (air gasification of resid vs coal).
- LC-Fining of vacuum bottoms for both desulfurizing and demetallizing[34] is a potentially attractive route to hydroprocessing for transportation fuel production.
- Air-blown gasification of resid is competitive with regenerable CAFB, so a Texaco partial oxidation system with preheated air feed, which has been successfully operated in a 1 MW pilot plant at Montebello, California, can provide clean fuel gas to a refinery distribution system, which CAFB cannot do.

Our conclusion from the economic assessment summarized above is that no definable market exists for CAFB.

POTENTIAL

The development program for CAFB was funded by EPA to investigate the possibility of a boiler pollution control system functioning to

Table 18

COST COMPARISON

	$/bbl EQUIVALENT	
	GCA	Westinghouse
Regenerable CAFB	5.90	5.90
Regenerable FGD	2.63[a]	4.70[b]
Nonregenerable FGD	2.40	3.02
LC-Fining	3.84	3.68
Coal Liquefaction	-	15.60
O_2/Coal Gasification	-	17.70
Air/Coal Gasification	-	9.67
O_2/Resid Gasification	-	17.70
Air/Resid Gasification	-	5.56

[a]Mag-Ox
[b]Wellman-Lord

clean the fuel and not the products of combustion.[1] The initial estimates for the CAFB retrofit to a 600 MW power boiler indicated "as much as 50% less" capital cost "than an add-on wet scrubbing system" for a residual-oil-fired installation.

In 1975, after a thorough assessment of the data from CAFB tests at the Esso-UK 750 kW unit in Abingdon, England, and after a 50 MW retrofit design for a CAFB system had been prepared by Stone and Webster, Inc., for New England Electric Systems,[3] it was apparent to us that "CAFB is 25 to 50 percent greater" in capital cost than "limestone scrubbing -- stack gas cleaning costs." Also, we concluded in 1975 that a larger hydrodesulfurization unit could treat vacuum bottoms with low metals content competitively with CAFB. Thus, the feedstock appropriate for CAFB was narrowed to high-heavy-metals-content residua because such material could not be fired in a stack-gas-scrubber-equipped boiler

because of corrosion/deposition problems and could not be hydrodesulfurized because of catalyst deactivation by the heavy metals in the residua.

Now, in 1979, CAFB continues to be evaluated as more expensive than stack-gas scrubbing. Several relatively new hydrodesulfurization processes, however, are reported to be capable of processing high heavy metal residuum. One of these, LC-Fining, was concluded by GCA to have lower processing costs for residuum cleanup than CAFB in their report to EPA.[3] It, thus, appears that processing any residual oil for pollution control can best be done by other than CAFB means. Also, the availability of residual oils for CAFB feedstock is dissappearing since the oil industry has both the ability and the urgent need to process all of their by-product distillates into transportation fuels to

- Reduce imports of oil
- Provide hydrogen for hydroprocessing
- Provide fuel gases for process equipment
- Meet increasing worldwide demand for distillate fuels
- Assure adequate domestic U. S. supplies of gasoline, diesel fuel, jet fuel, and home heating oil.

The potential application of CAFB to solid fuels (lignite, tire shreds, etc.) has yet to be satisfactorily demonstrated. In any case, air-blown gasification with core gas desulfurization is indicated to be competitive with CAFB and can supply clean, basically distributed fuel gas (within utility site or refinery site battery limits) to a large single boiler or to a multiplicity of units such as process heaters, steam reformers, and hydrotreaters. We conclude that the only possible market for CAFB may be a special situation where a suitable feedstock, not directly combustible, and an existing gas-fired boiler of moderate size, exist in the same size.

ENVIRONMENTAL IMPACT

The major environmental concerns associated with the CAFB process are SO_x, nitrogen oxide (NO_x), particulate control, solid waste disposal, and resource utilization.

The ability to control SO_x emissions has been partially demonstrated by the ERCA CAFB pilot unit operated in the regenerative mode, using liquid fuels and limestone sorbents. Integrated regenerative operation with sulfur recovery has not been performed. Only limited SO_x emission data using solid fuels have been collected on the pilot unit. While the ability of the CAFB demonstration plant to control the SO_x emissions is uncertain (e.g., the sulfur capture efficiency of the RESOX process and the ability to operate the demonstration plant regeneratively using solid fuels), it is likely that acceptable levels of SO_x control can be achieved with the CAFB process by selecting appropriate design and operating conditions. Once-through sorbent operation - rather than regenerative - may be required with some fuels.

Nitrogen oxide emissions from the CAFB process should be acceptable if the proper burner design is selected. Previous CAFB pilot unit operation has indicated low NO_x emission levels.

In the CAFB process particulate emissions are more a problem of process operability (i.e., deposition and erosion) than they are of environmental protection. Existing technology can reduce the particulate from a CAFB retrofited boiler to acceptable levels. If the gas passes through high-temperature cyclones before entering the boiler, particulate emissions will probably be only partially reduced and, in order to satisfy environmental standards, an electrostatic precipitator or baghouse will still be required after the gas exits from the boiler.

Westinghouse has investigated the environmental impact of the disposal of unprocessed and processed CAFB solid waste extensively. On the basis of laboratory testing results, we judged that the unprocessed CAFB

spent sorbent would be environmentally unacceptable for direct land disposal. Available test data, however, show that environmental acceptability can be achieved by further processing.

The major environmental concerns for direct disposal are heat release, sulfide, pH, calcium, sulfate (SO_4), and total dissolved solids (TDS). The major environmental concerns about disposal after processing are pH, calcium, SO_4, and TDS.

Results suggest that the disposal of processed CAFB solid waste may cause environmental effects comparable to (due to its chemical properties) or perhaps less negative than (due to its physical properties) the disposal of the residue from the currently commercialized FGD process.

Several processing techniques for CAFB solid residues have been identified, including both high-temperature and low-temperature options.

Although on the basis of its leachate quality the high-temperature processed compact appears to be environmentally superior to the other alternatives, the energy requirements would have to be evaluated in relation to the benefits. On the basis of environmental impact, dry sulfation would be the recommended process, followed by dead-burning and low-temperature fly ash blending.

As a subsystem, dry sulfation is the most expensive option, either as a percentage of plant cost or relatively, but its ultimate cost advantage results from elimination of a sulfur recovery plant. Back-up options are direct disposal, which is attractive if a consumer is able to utilize the material, and briquetting. The direct disposal option, with utilization of the material in building block, for example, is an option for the CAFB demonstation plant in San Benito, Texas.

The CAFB process provides some potential environmental benefits in the area of resource utilization. Some low-quality fuels suitable for consumption in the CAFB process are not easily utilized by conventional

technology. Such fuels represent an energy resource that should be utilized in the most effective manner, which in some cases may be gasification in the CAFB process.

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APPENDIX A

ATTRITION IN THE BUBBLING ZONE OF A FLUIDIZED BED

All of the studies relating to attrition in the bubbling zone are described in Appendix A.

ATTRITION IN THE GRID ZONE OF A FLUIDIZED BED

Attrition Mechanisms

The frequently considered source of attrition in a fluidized bed is the obvious grinding and shattering collisions of particles. There are several causes of particle wear, which include the following:

Abrasion

In this process defects, edges, and corners are knocked from particles by low-energy collisions. Abrasion can occur during passage of a gas bubble through the bed of solids.

High-Energy Collisions

Particles may be accelerated to high velocity; for example, when entrained in a jet at the distribution plate, the high-velocity particle can strike another particle or vessel wall and shatter into relatively large fragements.

Blinichev, Strel'tsov, and Lebedeva[A1] have distinguished two zones in a fluidized bed - the lower, which they call the "nozzle" effect zone, in which gas jets accelerate large particles to energies sufficient for shattering; and the upper zone, characterized by intensive mixing and low-energy impacts that grind particle surfaces.

Thermal Shock

When cold particles are added suddenly to a bed of red-hot solids there is severe thermal stress on the cold particles. One expects spalling of the particle surface and perhaps shattering of the entire particle into large fragments.[A2]

Chemical Stress

Sorbent particles calcine, then react with sulfur dioxide (SO_2); calcium oxide (CaO) forms calcium sulfite ($CaSO_3$), with subsequent changes in the lattice structure. This change in particle structure at its surface hardens particles in some cases, or in other cases causes internal stresses leading to spalling or weakened particle surfaces.[A2-A4]

Internal Gas Pressure

When cold limestone or dolomite makeup sorbent is added to a hot fluidized bed, the resulting calcination generates carbon dioxide (CO_2) within the particle. Esso Research Centre in Abingdon, UK (ERCA) found that a slower calcination rate of fresh limestone results in lower production of fines.[A5] Similarly, water within particle cracks will flash when heated to bed temperatures. While CO_2 pressures are moderate (100.0 kPa equilibrium at 900°C), steam pressures are high and can explode particles.

Transfer Lines and Cyclones

These are not a part of the fluidization process but are generally included in a fluidized-bed system. Sorbent breakage rate is related to the circulation rate of the solids and is controlled by equipment design effects on solids impact.

Kutyavina and Baskakov explain, "With fluidization, particles are ground by abrasion and splitting... Abrasion is evidently predominant even for brittle and insufficiently strong materials."[A6]

Similarly, Wei describes two mechanisms of particle attrition:

> 'grinding' or the abrasive removal of a layer of crystallites and matrix from the skin, and 'shattering' or the deep disintegration of the matrix material.

The former mechanism leaves behind a large particle somewhat reduced in size and a pile of very fine particles; the latter mechanism leaves an assortment of fragments from the very small to the very large. The former is controlled by the hardness of the crystallites and the abrasion resistance of the matrix; the latter is controlled by the impact elasticity of the matrix and imperfections in the structure.[A7] Doheim, Ghaneya, and Rassoul[A8] observed with fluidized iron ores in a nonreacting system that the primary mechanism of attrition is by abrasion, not breakage. Blinichev and others[A1] report that the wear of hard fluidized particles is by abrasion; soft materials split, then abrade. Forsythe and Hertwig[A9], Kutyavina and Baskakov,[A6] Zenz[A10] make the same observation.

In this report we have limited discussion to only the first source of attrition, grinding caused by rising gas bubbles in a fluidized bed. In most fluidized beds several attrition mechanisms will act. In this study we eliminated the grid (distribution-plate) jets by using a porous, sintered-metal grid and avoided temperature and chemical effects by operating at room temperature. Energy collisions also occur above the bed where particles splash into the freeboard as bubbles break.

EXPERIMENTAL STUDIES

Table A1 presents an index of experiments carried out.

Table A1

INDEX OF EXPERIMENTS

Experiment Title	Purpose	Apparatus	Reported in	
			Section of This Report	Monthly Report for
Jet Observations in a Semicircular Bed	Observe the character of solids flow into a jet	7- and 20-cm semicircular bed		1/78, 2/78
Dependence of Jet Length on Orifice Dimensions and Particle Diameter	Determine jet lengths to avoid unnecessary depth of cover solids and thus minimize unwanted bubbling-bed attrition	7-cm circular fluidized bed		2/78
Measurement of Particle Material Strength in a Circulating Bed	Provide relative measures of stone attrition resistance in jet attrition	7-cm circular fluidized bed		
Measurement of Particle Material Strength in a Jet without Circulation	Measure the hardness of particle material by extent of attrition where particles hit a target only once and do not recirculate	Target impaction device		3/78, 4/78
Measurement of Variation in the Composition of Calcined Limestone	Determine if the composition of limestone varies between small particles	Wet chemical assay		Not reported
Measurement of Attrition Attributed to Grid Jets	Investigate and describe attrition in the vicinity of a grid	7-cm circular fluidized bed		Not reported
Testing for Attrition Tendency of Fluidized-Bed Gasification Sorbents	Develop an apparatus and procedure for screening sorbents on the basis of attrition tendency	10-cm circular, high-temperature fluidized-bed system	Appendix	

First Experiment: Jet Observations in a Semicircular Bed

Rationale and Purpose

An unknown in grid jet attrition is the character of particle entrainment into a jet. The purpose of these experiments was to observe the flow of particles toward and into a jet.

Apparatus

In these experiments we used a semicircular transparent cell, 7-cm in inside diameter. The apparatus shown in Figure A1 has one semicircular orifice.

Procedure

The apparatus was used for observing the circulation of particles in a jet. We filmed motion and trajectories in 7- and 20-cm-id semicircular beds. About one percent of the bed particles was colored red to clarify the motion of individual particles.

Dwg. 7692A08

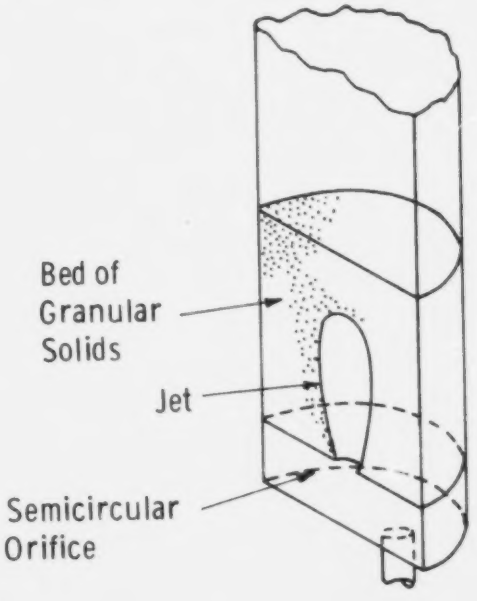


Figure A1. Semicircular Jet Model

Results

The product of this study was close-up films of particle motion in the vicinity of a jet. Repeated viewing of the films revealed that:

- There is no small-scale turbulence in the bed of particles except very close to the jet. Bed particles follow smooth, parallel trajectories.
- Particles follow roughly elliptical trajectories starting at the top of the jet. Particles migrate to the jet and are entrained and delivered by the jet to its top, where they begin another circulation.
- We observed an envelope such as Merry[All] described enclosing the jet circulation region (Figure A2).

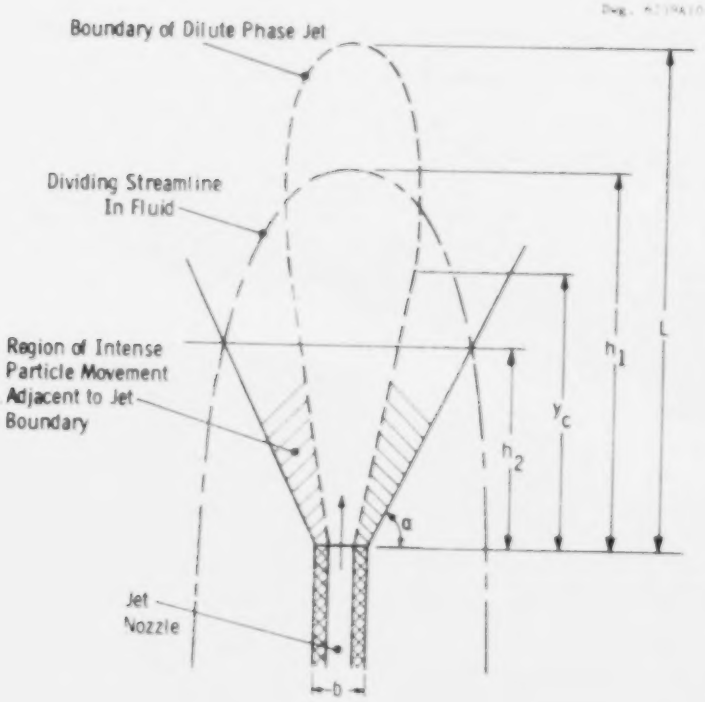


Figure A2. Graphic Representation of the Interaction of Particle and Fluid Flow Fields in the Vicinity of the Jet

Discussion

Inspection of these films verified the complexity of particle circulation and attrition in the region of a jet. None of the rates is described for particle entrainment and circulation. Study and description of particle circulation rates, entrainment rates, and local attrition rates will be needed for a basic understanding of grid jet attrition. For this study we decided to concentrate on a statistical approach to defining grid jet attrition rather than to investigate the interconnected complex of mechanisms.

Conclusions

- Solids are entrained into a jet over its entire length.
- The density of solids in a jet increases with height above the orifice.
- The mass flow of entrainment into a jet is constant over its length. The mass flux ϕ (mass/area/time) decreases with height approximately as $\phi = \phi_o (1-X/L)$, but since the jet diameter increases with distance measured along its axis, the mass inflow is about constant.
- Particles entrain in the jet, smash into the roof of the jet, and recirculate down the jet cavity side in a free-flowing boundary layer.

Second Experiment: Dependence of Jet Length on Orifice Diameter and Particle Diameter

Rationale and Purpose

Because grid jet attrition occurs on a per-jet basis, measurement of the attrition rate (grams per jet per hour) should include only the jet with a minimum of surrounding bed material subject to attrition by bubbling. Because we wanted to know jet length in our apparatus to allow a minimum cover of solids over the jet, we measured jet length for several orifices in the 7-cm-id column.

Apparatus

The 7-cm-id attrition test cell used in this experiment is pictured in Figures A3 and A4. It accepts interchangeable grids with a single orifice.

Procedure

We filled the cell to a measured depth and increased the gas flow rate very slowly until the jet broke through the bed surface.

Results

Figures A5 and A6 show the results of these jet length measurements. All of these curves have positive slopes, affirming that a greater grid, ΔP, increases gas flow and causes a longer jet. Similarly, increasing the orifice diameter causes a longer jet. We measured jet length in beds of two particle sizes (dp). For the particle sizes tested, 500 to 710 μm and 1000 to 1410 μm, the jet length is about inversely proportional to particle diameter.

Conclusions

We can conclude from Figures A5 and A6 that:

- Jet length is about proportional to grid ΔP.
- Jet length is about inversely proportional to particle diameter for a given material and grid ΔP.
- Jet length increases with increasing orifice diameter.

We have drawn these conclusions from limited experiments. They apply only to the conditions encountered in this apparatus; the results are not generally applicable.

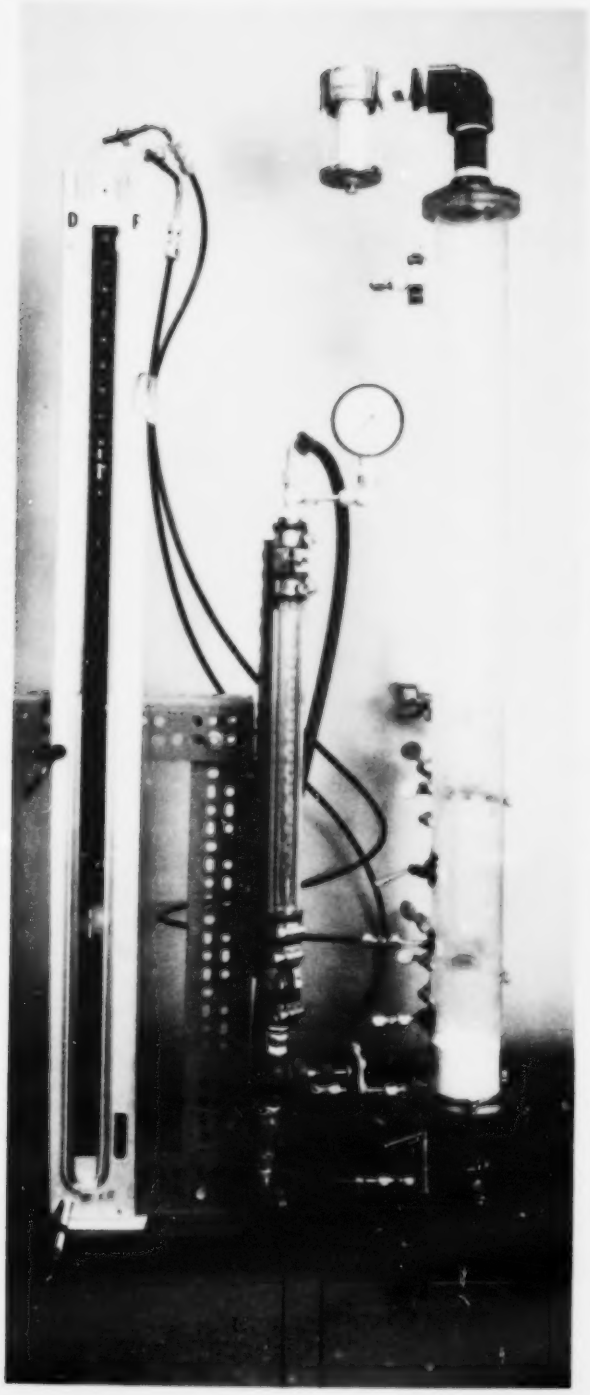


Figure A3. Overall Photo of Attrition Test Cell

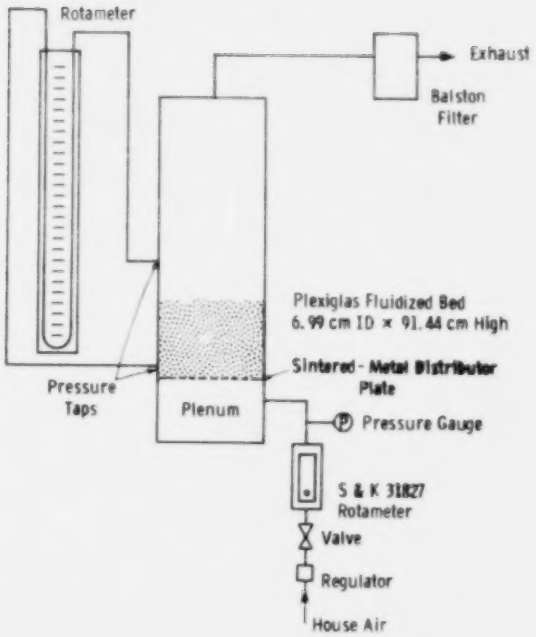


Figure A4. Flow Diagram for Room-Temperature Fluidized Bed

Third Experiment: Measurement of Particle Material Strength in a Jet with Circulation

Purpose

In the process of grid jet attrition, particles entrain into the high-speed jet, accelerate, and smash into the roof of the jet. We hypothesize that soft materials (such as chalk) will attrite readily and hard materials (such as diamonds) will attrite slowly; in other words, attrition rate varies inversely with particle strength. The purpose of this experiment was to assign a measure of particle hardness to several materials ranging from very soft to very hard.

Apparatus

The test apparatus was the 7-cm-id test cell (Figure A3) fitted with the orifice-and-target device shown in Figures A7 and A8. In this ment the orifice diameter was 0.257 cm.

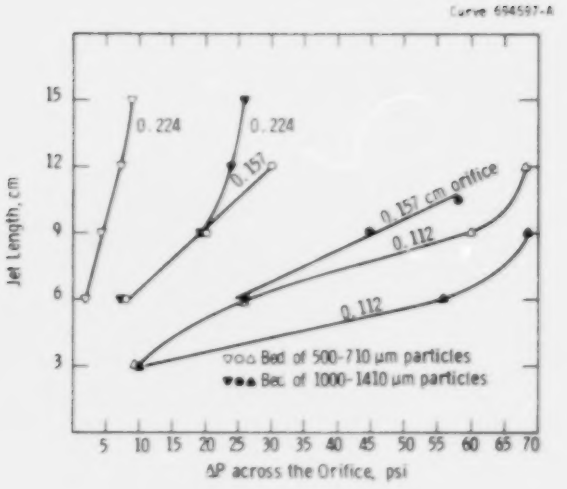


Figure A5. Jet Lengths in Beds of Tymochtee Dolomite as Affected by Grid ΔP, Orifice Diameter, and Stone Particle Diameter, 18°C

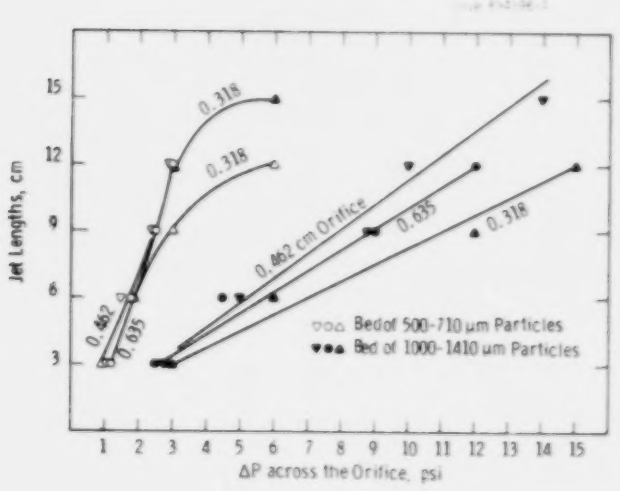


Figure A6. Jet Lengths in Bed of Tymochtee Dolomite as Affected by Grid ΔP, Orifice Diameter, and Stone Particle Diameter, 18°C

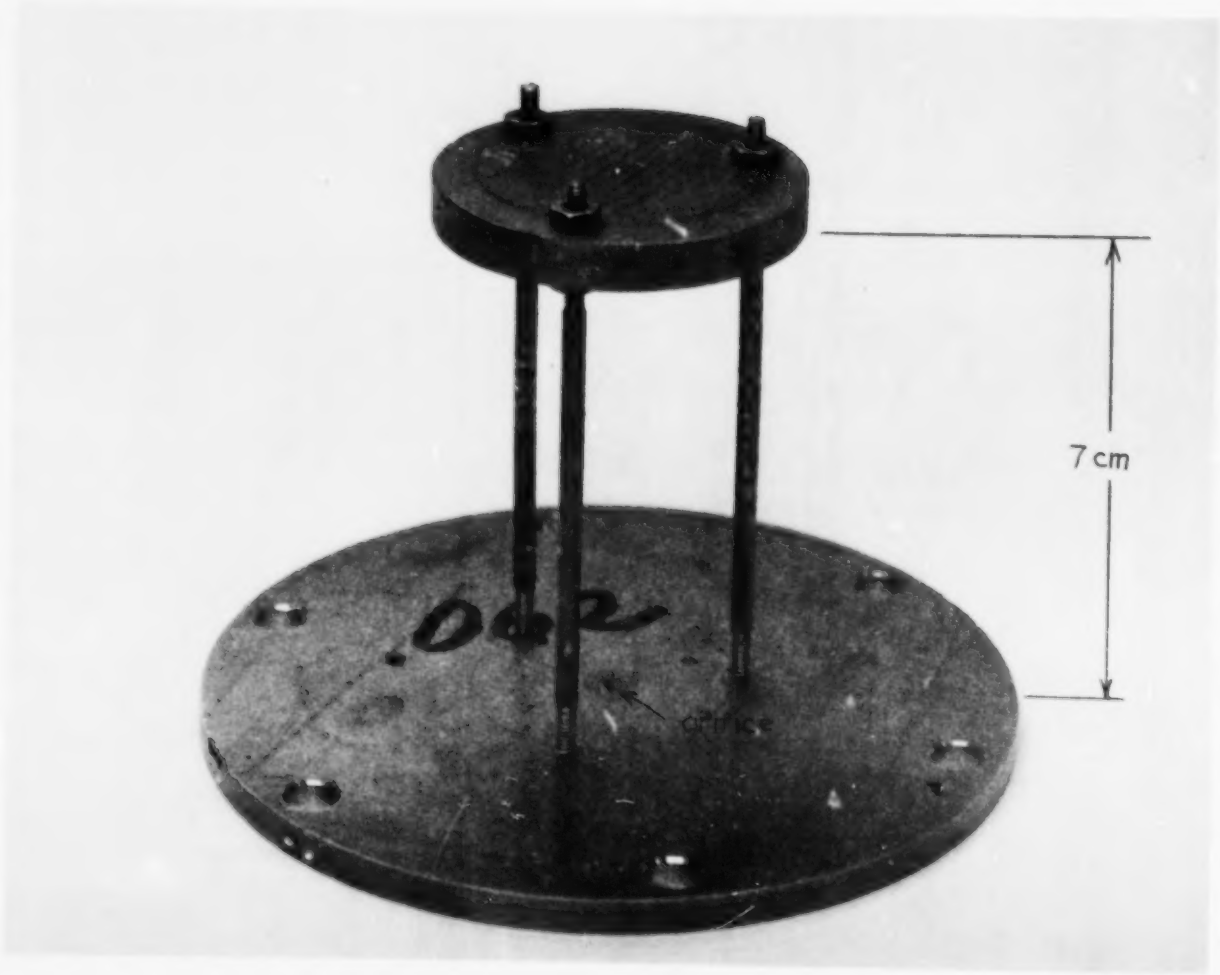


Figure A7. Jet-and-Target Device for Measuring Particle Strength

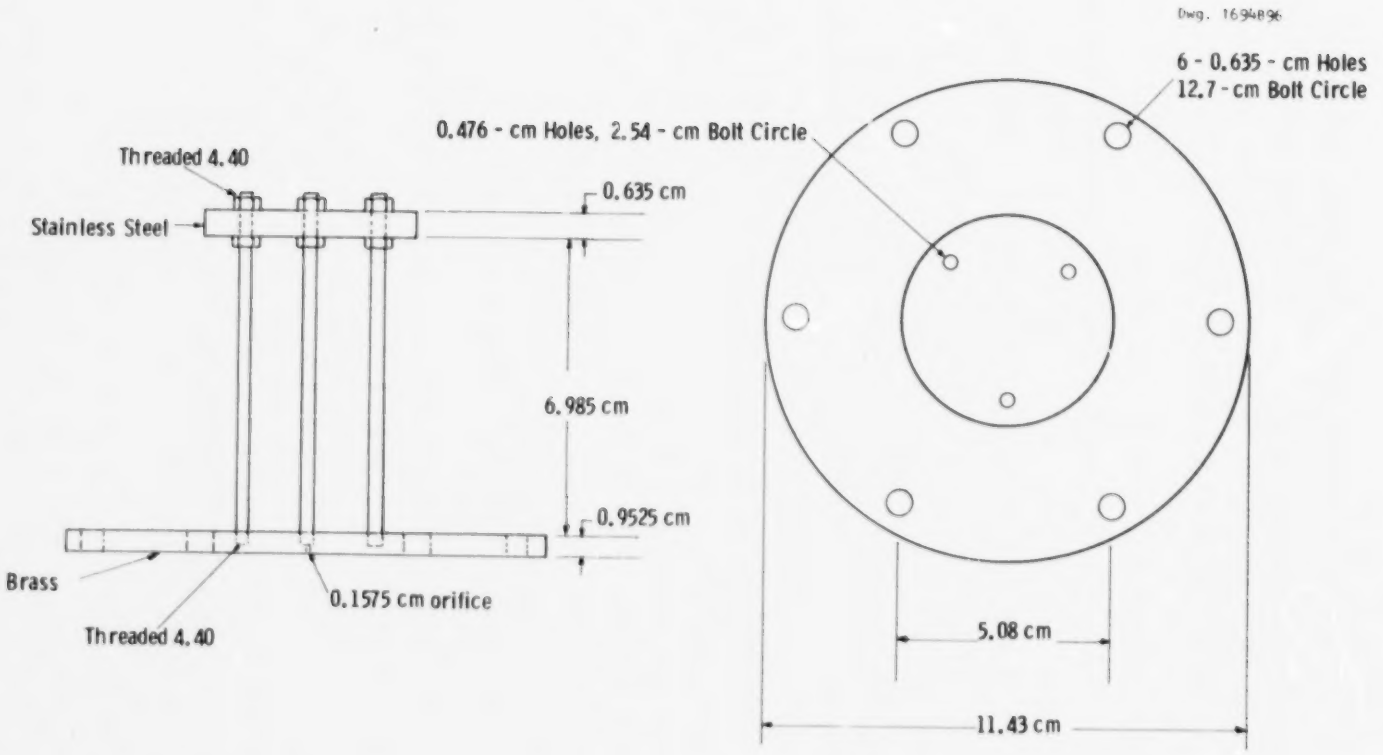


Figure A8. Target Assembly for 7-cm Attrition Cold Test Cell

Procedure

The procedure in these tests was to charge the test cell with 1000 to 1410 μm ground stone to a depth of 9 cm, turn on the gas flow to a plenum pressure of about 100 kPa gauge, and allow the jet to operate for 5.0 minutes. The detailed test procedure was:

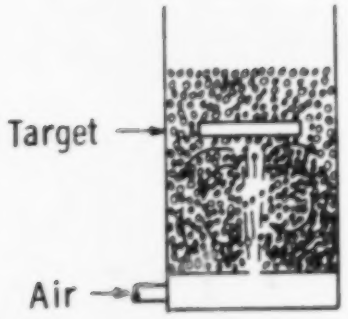
- Presieve all stone to 1000 to 1410 μm.
- Place filter in 100°C oven for 1 hour, cool in desiccator for 1/2 hour, and weigh.
- Assemble 7-cm bed with the orifice and the 5.1-cm-diameter target 7.0 cm above the orifice.
- Place presieved stone in 100°C oven for 1 hour, cool in desiccator for 1/2 hour. Weigh.
- Fill bed to a total depth of 9 cm with stone and weigh.
- Install filter on bed exhaust.
- Set rotameter to 65 percent. Run for 5.0 minutes. Record plenum pressure and rotameter pressure.
- After test remove filter, dry in 100°C oven for 1 hour, cool in desiccator for 1/2 hour, and weigh.
- Remove stone from bed at 100°C for 1 hour, cool in desiccator for 1/2 hour, weigh.
- Perform sieve analysis on recovered solids.

We removed the solids from the system and carefully measured the size distribution of the product.

Results

The motion of solids in the jet attrition apparatus was evident when we reviewed particle motion through the clear plastic cell. Particles could be seen circulating downwards as shown in the inset figure.

Dwg. 7692A07



Results of these tests are listed in Table A2 and in Figures A9 and A10. Figure A10, which shows the differential size distribution on an arithmetic frequency ordinate, clearly shows the relative amounts of attrition products. The softer stones, tuff and marble, attrited more severely after 5.0 minutes of jet action; the effect on the harder aplite and diabase was much less noticeable. For all four minerals the mode (peak) of attrition products we conjecture is at about 50 μm, with marble showing an additional mode at 300 μm. We conjecture these modes to be related to grain or crystallite sizes. Table A2 summarizes sieve analysis data and lists the specific surfaces of powders. Specific surface data are based on the entire charge of powder, with an assumed particle diameter of 10 μm for lost powder. We analyzed filter fines from the tuff attrition by Coulter Counter®. The logarithmic median diameter was $\phi = 7.1$ (7.5 μm), with a deviation measure of $\phi = 1.24$. The Hazen effective sand size of filter fines was 1.95 μm (fine silt), with a uniformity coefficient of 4.77.

During the tests, the pressure drop averaged 212-101 = 111 kPa across the 0.257-cm diameter orifice.

Discussion

These results suggest that we can differentiate between stone types; we can identify the easily attritable and hard-to-attrite materials. The specific surface, a, and mean diameter, d_{gv}, are related

Table 2

SUMMARY OF SIEVE ANALYSES AND POWDER STATISTICS AFTER 5.9 MINUTES OF JET ATTRITION WITH A 0.256-cm JET

Stone Type	Before	After Fluidization			
	All	Tuff	White Marble	Aplite	Diabase
Specific Gravity g/cm³	(Same as after)	1.53	2.18	2.40	2.88
Qualitative Hardness	(Same as after)	Soft	Soft	Hard	Hard
Specific Surface, 10^6 cm^{-1}	50.4	571	164	96.5	80.0
Mean Diameter, cm*	0.119	0.0105	0.037	0.062	0.075
% Wt Loss of Initial Size	0	43.8	36.3	18.1	15.0

Sieve Size, D_2-D_1 µm	Mean Diam.	Fraction	Frequency**	Grams	Frequency**	Grams	Frequency**	Grams	Frequency**	Grams	Frequency**
1410 - 2000	1680	0	0	1.20	0.0135	14.40	0.0997	3.80	0.0224	7.10	0.0400
1000 - 1410	1190	1.00	2.89	143.70	1.6123	251.70	1.7424	345.20	2.3442	428.30	2.4158
710 - 1000	840	0	0	40.68	0.4564	45.54	0.3153	44.12	0.2996	46.00	0.2595
500 - 710	595	0	0	5.16	0.0579	14.60	0.1011	8.97	0.0609	7.58	0.0428
355 - 500	420	0	0	3.04	0.0341	15.96	0.1105	6.60	0.0448	5.50	0.0310
250 - 355	300	0	0	2.20	0.0247	20.17	0.1396	4.75	0.0323	4.56	0.0257
125 - 250	180	0	0	3.60	0.0202	28.81	0.0996	5.00	0.0170	5.12	0.0144
63 - 125	90	0	0	6.60	0.0370	13.83	0.0478	2.98	0.0101	3.36	0.0095
43 - 63	52	0	0	19.72	0.2213	7.23	0.0501	2.24	0.0152	3.77	0.0213
30 - 43	36	0	0	19.16	0.2150	3.34	0.0231	0.76	0.0052	0.36	0.0020
Filter + Losses	10	0	0	12.54	0.0221	1.92	0.0021	1.68	0.0018	0.75	0.0007

* $(\Sigma\ fi/Dpi)^{-1}$ ** Frequency = Fraction/$\ln(D_2/D_1)$

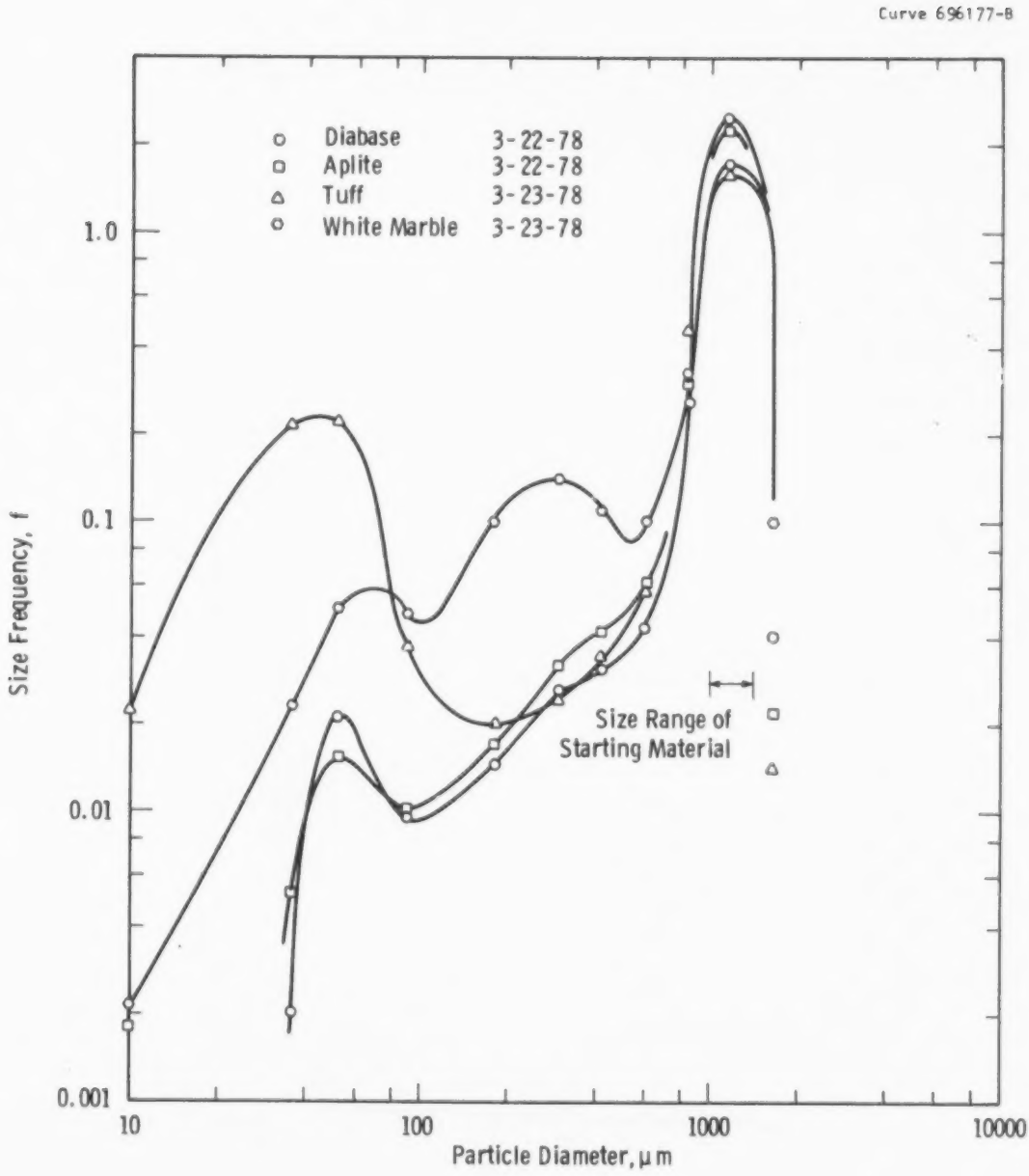


Figure A9. Size Frequency Distribution Curves for Attrition Hardness Testing of Several Minerals. Logarithmic Ordinate. f = fraction on sieve ÷ $\ln(d_{pmax}/d_{pmin})$

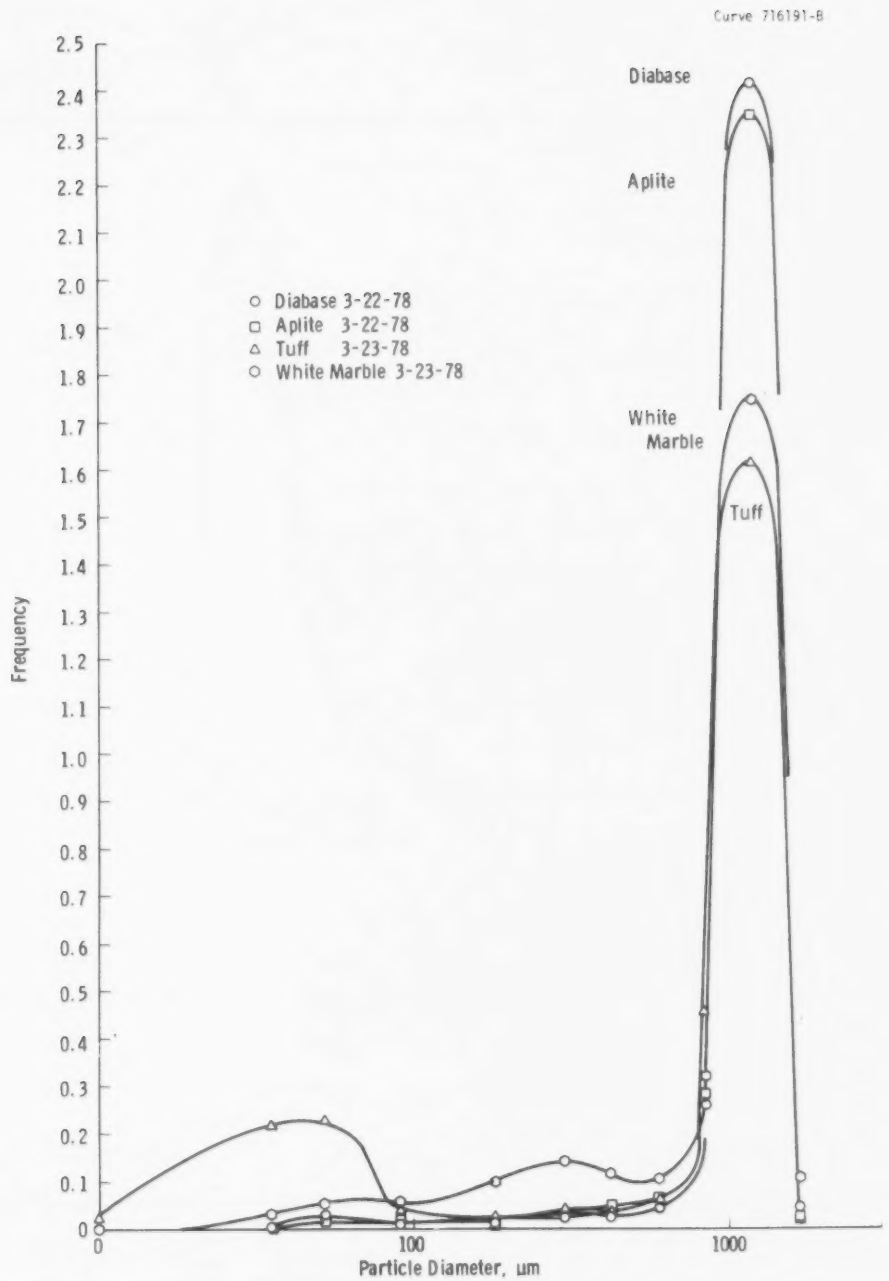


Figure A10. Size Frequency Distribution Curves for Attrition Hardness Testing of Several Minerals. Logarithmic Ordinate. f = (fraction on sieve) ÷ (Δ ℓnd_p)

by $d_{sv} = 6 \div a$. There is no formula relating the mean diameter of solids after jet attrition and the percent of solids reduced smaller than the starting sieve size. When compared on a graph (Figure A11). however, the diameter d_{sv} and percent loss of coarses* correlate well; they are related by the regression line

$$\% \text{ loss of coarses} = 50.5 - 480.3\ d_{sv}, \qquad r = 0.980$$

for $0.0105 < d_{sv} < 0.0750$ cm. This correlation means that we can determine the easily measured percent loss of coarses and obtain a precise measure of either the mean particle diameter or the specific surface of the powder.

Curve 716190-A

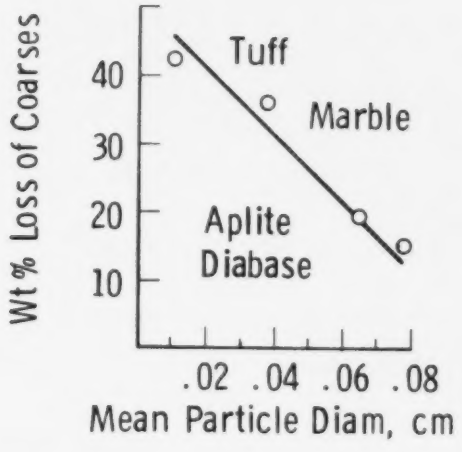


Figure A11 - Relation between Loss of Coarses and Final Particle Diameter

*Coarses (as opposed to fines) are solids in the largest sieve class, 1000 to 1410 μm.

Stone strength values (attrition resistance) are calculated from this summary of Table A2.

	Stone	Specific Surface ($cm^{-1} \times 10^6$)	Increase over "before"
Before Treatment	All stones	50.4	0
After Treatment	Tuff	571	521
	White marble	164	114
	Aplite	96	46
	Diabase	80	30

We calculated the change in specific surface for each stone after five minutes of attrition in a single jet. Increases in specific surface for the four types of stone are

Tuff	Marble	Aplite	Diabase
521	114	46	30

Relating these values to that of tuff = 100, the softest mineral gives

100	21.9	8.8	5.8

These values are relative measures of ease of breakage. Their inverses measure stone strength.

100	457	1132	1740

We chose tuff and marble as the two solids for study in the grid-jet attrition tests. Their relative hardnesses taken as

$$\frac{\sigma}{\rho} \text{ Tuff} = 100$$

$$\frac{\sigma}{\rho} \text{ Marble} = 457$$

are sufficiently different, and both are in the same hardness range as calcined limestone sorbent.

Conclusions

- Single jet attrition testing of different minerals gives increases in specific surface (or loss of coarse particles or decrease in mean particle diameter) in the ranking expected.
- The attrition fragments for the four minerals tested have modes at about 50 μm. White marble shows a second mode at about 300 μm. These modes are conjectured to be related to the diameters of grains or crystallites comprising the minerals.
- The mean particle diameter (inverse of specific surface) correlates linearly at 98 percent with the loss of coarse particles in the orifice-and-target apparatus.
- Tuff and marble are two minerals well suited to jet attrition studies. Their measures of hardness or attrition resistance are sufficiently different, and both have hardnesses comparable to those of calcined limestone or dolomite.

Fourth Experiment: Measurement of Particle Material Strength in a Jet without Circulation

Purpose

The apparatus and procedure described in the third experiment measures the relative strength of circulating particles. The rate of attrition depends on both the particle strength and the rate of

circulation. This procedure provides a measure of particle strength as related to the jet where particles do, indeed, circulate but does not give a measure of particle strength alone.

The purpose of this experiment was to measure the relative strength (attrition resistance) of minerals when attrited by a single impact against a target.

Apparatus

Figure A12 shows the apparatus used in this experiment. Its purpose is to accelerate particles to near-sonic velocity and shoot them against a target, thus providing a measure of particle strength.

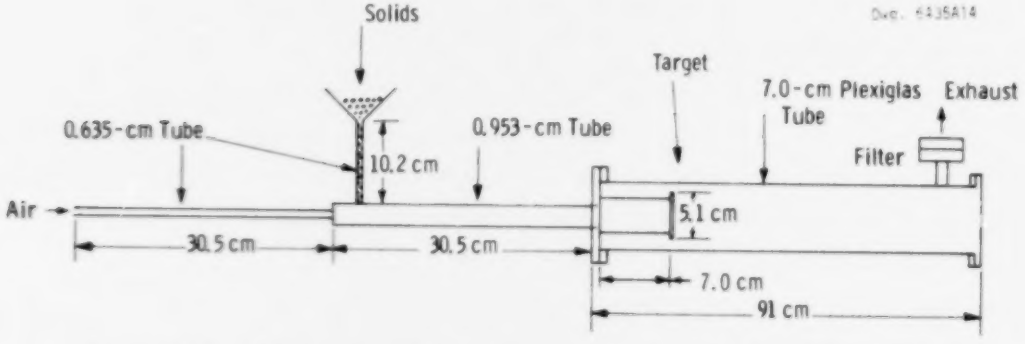


Figure A12 - Apparatus for Measurement of Particle Strength in a Nonrecirculating System

Procedure

The test procedure in this experiment was to

1. Presieve all stone - 12 + 16 U. S. mesh.
2. Place filter in 100°C oven for one hour; place in desiccator for one-half hour.
3. Assemble 7-cm bed with target and stone injection system.
4. Place presieved stone in 100°C oven for one hour; place in desiccator for one-half hour. Weigh.
5. Place 100 g of stone in funnel.

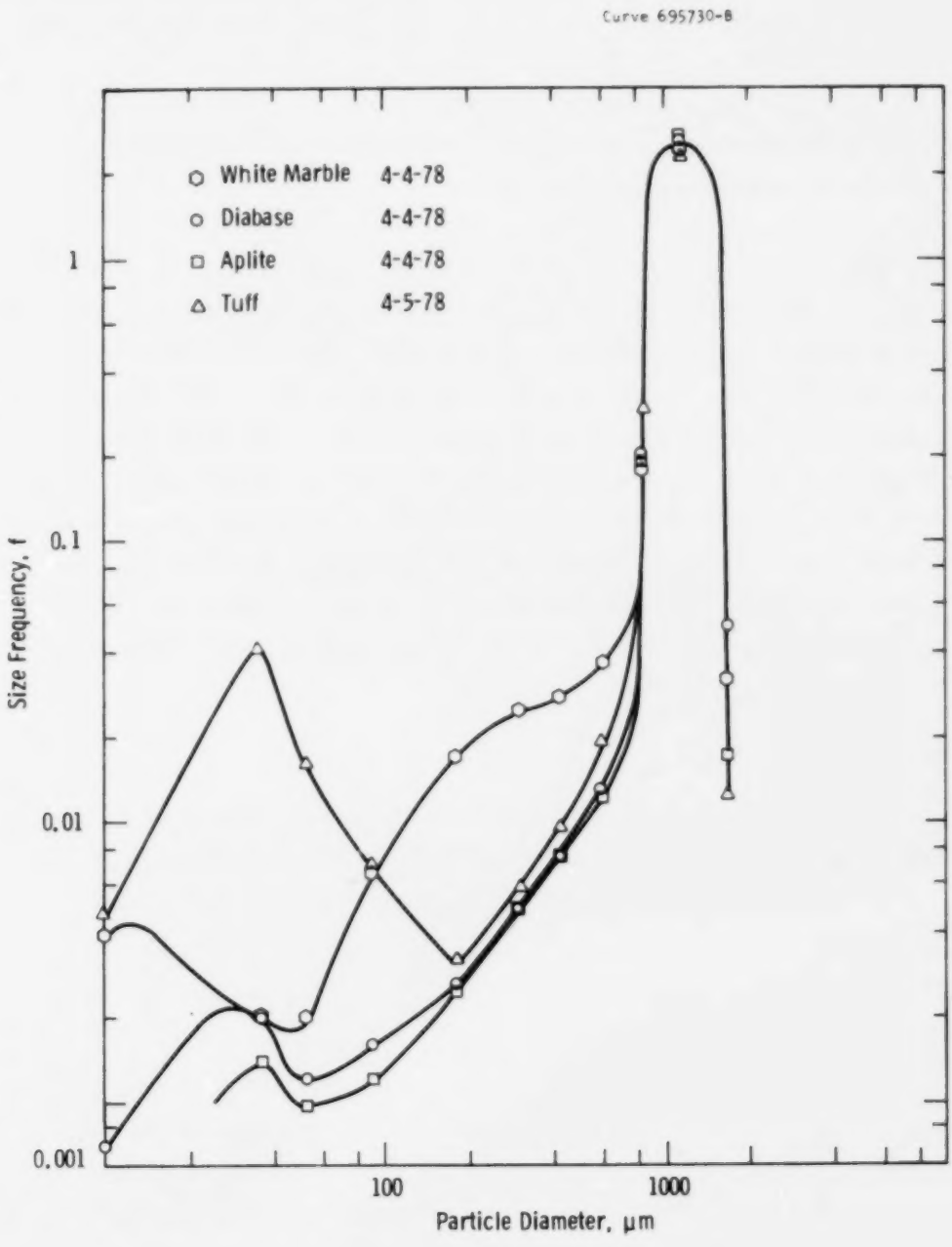


Figure A13 - Size Frequency Distribution for Impingement of a Stream of Nonrecirculating Particles against a Target

6. Install filter on bed.
7. Set rotameter to Z = 75.
8. After test remove filter and stone. Place in 100°C oven for one hour; place in a desiccator for one-half hour. Weigh.
9. Sieve and analyze attrition products.

Results

Results of testing for particle attrition by impingement on a plate are listed in Table A3 and graphed in Figure A13. As in the third experiment, the tangibly softer stones, tuff and marble, attrited more than did the harder aplite and diabase. Again, there is a mode near 50 μm (30 μm in this experiment) and a second mode for marble (more of a shoulder in this experiment) near 300 μm. Table A3 summarizes frequency data and lists the specific surface and surface-volume diameter d_{sv} for solids after treatment. The mass balances in this experiment were very close, all within 100 ± 0.9 percent. Detailed sieve analysis data are listed in Table A4.

Discussion

As in the third experiment, we compared the weight % loss of coarses with the mean particle diameter of the attrited solids. Figure 14 shows that the produce diameter d_{sv} and percent loss of coarses correlate closely as

$$\% \text{ loss of coarses} = 17.9 - 93.3\ d_{sv}, \qquad r = 0.971$$

for $0.041 < d_{sv} < 0.109$ cm.

Figures A11 and A14 are not directly comparable as they involve different mechanisms; the fluidization mechanism is dependent on time, the single-impact-jet mechanism is independent of time. Again, however, mean particle diameter d_{sv} and weight percent loss of coarses are closely related.

Curve 71o883-A

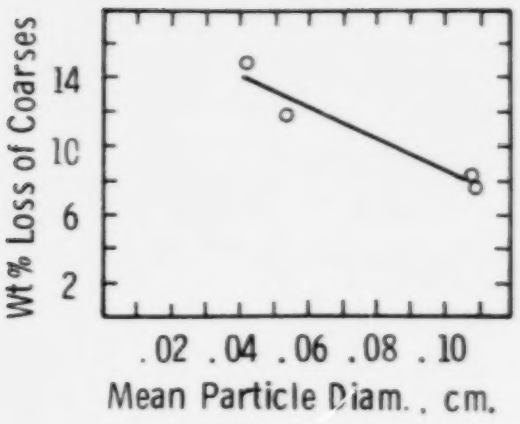


Figure A14. Relation between Loss of Coarses and Final Particle Diameter for High-Speed Impingement

Table A3

SUMMARY OF SIEVE ANALYSES AND POWDER STATISTICS AFTER SINGLE IMPACT OF PARTICLES AGAINST A TARGET

Stone Type		Before	After Treatment			
		All	Tuff	White Marble	Aplite	Diabase
Specific Gravity, g/cm^3		Same as after	1.53	2.18	2.40	2.88
Qualitative Hardness		Same as after	Soft	Soft	Hard	Hard
Specific Surface, cm^{-1}		50.4	146	113	55.1	55.7
Mean Diameter, cm*		0.119	0.041	0.053	0.109	0.108
% Wt Loss of Initial Size		0	14.9	11.9	7.5	8.2
Sieve Size, μm	Mean Dia., μm	Size Frequency				
1440-2000	1680	0	0.0145	0.0318	0.0173	0.0491
1000-1410	1190	2.8902	2.4451	2.5145	2.6561	2.6040
710-1000	840	0	0.2896	0.1789	0.1832	0.2000
500-710	595	0	0.0191	0.364	0.0116	0.0127
355-500	420	0	0.0095	0.0275	0.0072	0.0075
250-355	300	0	0.0058	0.0246	0.0049	0.0049
125-250	180	0	0.0032	0.0169	0.0025	0.0026
63-125	90	0	0.0072	0.0066	0.0012	0.0016
43-63	52	0	0.0162	0.0020	0.0009	0.0012
30-43	36	0	0.0405	0.0020	0.0014	0.0020
	10	0	0.0046	0.0039	0.0000	0.0000

*6/Specific Surface

**Fraction of powder mass within the size range $d \pm \Delta D = F(d) \ln \frac{d + \Delta d}{d - \Delta d}$

Table 4

DETAILED SIEVE ANALYSIS DATA FOR JET ATTRITION WITHOUT CIRCULATION

WT MAR 4-4-78

********** BEFORE **********
TOTAL f/D= 8.403361344538
1/TOTAL = .119
SPECIFIC SURFACE= 504201.6806723

T MESH	MASS	FRACT.	f/d	f/(lnD2/D1)
16	100.0000	1.0000	8.4034	2.8902

********** AFTER **********
TOTAL f/D= 18.82833620627
1/TOTAL = 5.31114374E-02
SPECIFIC SURFACE= 1129700.172376

T MESH	MASS	FRACT.	CUM FRACT.	f/d	f/(lnD2/D1)
12	1.1000	0.0110	1.0000	0.0655	0.0318
16	87.0000	0.8700	0.9890	7.3109	2.5145
24	6.2200	0.0622	0.1190	0.7405	0.1798
32	1.2600	0.0126	0.0568	0.2118	0.0364
42	0.9500	0.0095	0.0442	0.2262	0.0275
60	0.8500	0.0085	0.0347	0.2833	0.0246
115	1.1700	0.0117	0.0262	0.6500	0.0169
250	0.4600	0.0046	0.0145	0.5111	0.0066
325	0.0700	0.0007	0.0099	0.1346	0.0020
PAN	0.0700	0.0007	0.0092	0.1944	0.0020
F+L	0.8500	0.0085	0.0085	8.5000	0.0039

APLITE 4-4-78

********** BEFORE **********
TOTAL f/D= 8.403361344538
1/TOTAL = .119
SPECIFIC SURFACE= 504201.6806723

T MESH	MASS	FRACT.	f/d	f/(lnD2/D1)
16	100.0000	1.0000	8.4034	2.8902

********** AFTER **********
TOTAL f/D= 9.176497162962
1/TOTAL = .1089740433895
SPECIFIC SURFACE= 550589.8297776

T MESH	MASS	FRACT.	CUM FRACT.	f/d	f/(lnD2/D1)
12	0.6000	0.0060	1.0000	0.0357	0.0173
16	91.9000	0.9190	0.9940	7.7227	2.6561
24	6.3400	0.0634	0.0750	0.7548	0.1832
32	0.4000	0.0040	0.0116	0.0672	0.0116
42	0.2500	0.0025	0.0076	0.0595	0.0072
60	0.1700	0.0017	0.0051	0.0567	0.0049
115	0.1700	0.0017	0.0034	0.0944	0.0025
250	0.0800	0.0008	0.0017	0.0889	0.0012
325	0.0300	0.0003	0.0009	0.0577	0.0009
PAN	0.0500	0.0005	0.0006	0.1389	0.0014
F+L	0.0100	0.0001	0.0001	0.1000	0.0000

Table 4 (Continued)

TUFF 4-5-78

********** BEFORE **********
TOTAL f/D= 8.403361344538
1/TOTAL = .119
SPECIFIC SURFACE= 504201.6806723

T MESH	MASS	FRACT.	f/d	f/(lnD2/D1)
16	100.0000	1.0000	8.4034	2.8902

********** AFTER **********
TOTAL f/D= 24.33161495366
1/TOTAL = 4.10987927E-02
SPECIFIC SURFACE= 1459896.89722

T MESH	MASS	FRACT.	CUM FRACT.	f/d	f/(lnD2/D1)
12	0.5000	0.0050	1.0000	0.0298	0.0145
16	84.6000	0.8460	0.9950	7.1092	2.4451
24	10.0200	0.1002	0.1490	1.1929	0.2896
32	0.6600	0.0066	0.0488	0.1109	0.0191
42	0.3300	0.0033	0.0422	0.0786	0.0095
60	0.2000	0.0020	0.0389	0.0667	0.0058
115	0.2200	0.0022	0.0369	0.1222	0.0032
250	0.5000	0.0050	0.0347	0.5556	0.0072
325	0.5600	0.0056	0.0297	1.0769	0.0162
PAN	1.4000	0.0140	0.0241	3.8889	0.0405
F+L	1.0100	0.0101	0.0101	10.1000	0.0046

DIABASE 4-4-78

********** BEFORE **********
TOTAL f/D= 8.403361344538
1/TOTAL = .119
SPECIFIC SURFACE= 504201.6806723

T MESH	MASS	FRACT.	f/d	f/(lnD2/D1)
16	100.0000	1.0000	8.4034	2.8902

********** AFTER **********
TOTAL f/D= 9.282539323418
1/TOTAL = .1077291423347
SPECIFIC SURFACE= 556952.3594051

T MESH	MASS	FRACT.	CUM FRACT.	f/d	f/(lnD2/D1)
12	1.7000	0.0170	1.0000	0.1012	0.0491
16	90.1000	0.9010	0.9830	7.5714	2.6040
24	6.9200	0.0692	0.0820	0.8238	0.2000
32	0.4400	0.0044	0.0128	0.0739	0.0127
42	0.2600	0.0026	0.0084	0.0619	0.0075
60	0.1700	0.0017	0.0058	0.0567	0.0049
115	0.1800	0.0018	0.0041	0.1000	0.0026
250	0.1100	0.0011	0.0023	0.1222	0.0016
325	0.0400	0.0004	0.0012	0.0769	0.0012
PAN	0.0700	0.0007	0.0008	0.1944	0.0020
F+L	0.0100	0.0001	0.0001	0.1000	0.0000

We calculated the change in specific surface for each stone after impact in the jet. Increases in specific surface for the four types of stone are:

Stone	Tuff	Marble	Aplite	Diabase
Before	50.4	50.4	50.4	50.4
After	146.0	113.0	55.1	55.7
Increase	95.6	62.6	4.7	5.3

Relating these values to that of tuff = 100, the softest mineral gives:

100	65.5	4.9	5.5

These values are relative measures of ease of breakage. Their inverses (scaled up to tuff = 100) measure stone strength:

100	152.7	2034	1804

These values do differ from those measured in the circulating bed (Experiment 3):

100	457	1132	1740

but the correlation between measures of hardness is fairly good (Figure A15).

Curve 716189-A

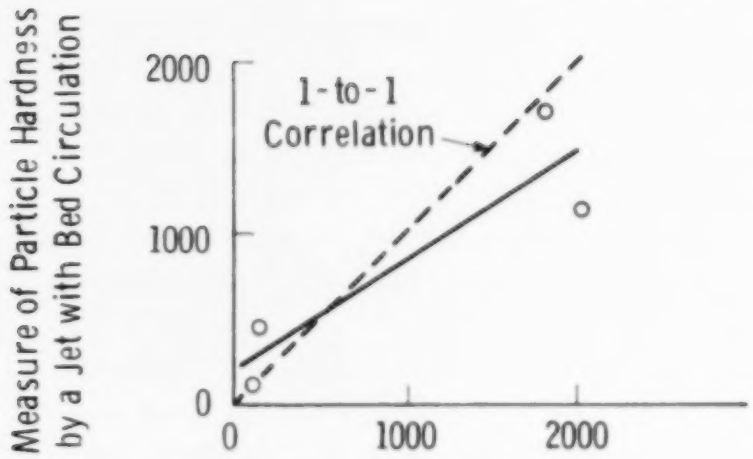


Figure A15. Measure of Particle Hardness by Single Impact from a Jet

We are confronted with two procedures for estimating material strength on impact. One procedure (preceding experiment) combines both particle strength and rate of circulation; the other (this experiment) eliminates rate of circulation and is affected primarily by particle strength. We believe that t'e procedure involving jet action in a bed of material (preceding experiment) is more pertinent. The rate of circulation is an integral part of the grid jet attrition mechanism. Since it cannot be measured separately by any simple test, the circulation rate is best included with the measurement of material strength.

Conclusions

- Particles injected into a horizontal jet and shot against a target plate attrited appreciably. Between 8 and 15 percent of the coarse solids were fragmented by a single impact.

- As in the jet attrition with circulation of a bed of particles the mode of fragment sizes was near 50 μm (30-40 μm in the experiment), with a second mode for white marble near 300 μm. Tuff fragments show a well-defined mode at 40 μm.
- The weight loss of coarse particles from a single high-speed impact is well correlated with the mean particle size of all attrited particles.
- Both methods of measuring particle hardness or attrition resistance (third and fourth experiments) give comparable results.
- We chose the method of measuring particle hardness in a circulating bed for the following experiments because the procedure is more like the action in a fluidized bed.

Fifth Experiment: Measurement of Variation in the Composition of Calcined Limestone

Purpose

In some TGA or wet chemical measurements a single particle of sorbent is tested. One assumes that the single particle epitomizes all particles.

After calcining limestone, however, we have noticed that some particles remain gray and others become white, as expected in dead-burning limestone. We separated and analyzed gray and white particles of calcined limestone to see if they differed in composition.

Procedure

We gathered several particles of each color about 1 mm in diameter and assayed them for chemical composition. Particles had been fluidized at 815°C for 100 hours in nitrogen.

Results

Results of the chemical assay are

Chemical Species	%	
	White Particles	Gray Particles
Carbon Dioxide	1.47	1.51
Calcium	64.96	4.75
Magnesium	0.39	0.00

Discussion and Conclusion

These results suggest that impurities are present in large aggregates, evidenced by both appearance (grayness or whiteness) and chemical composition. They further suggest caution in gathering small sorbent samples and the possible need to mill and split sorbents when a small (<1g) sample of solids is assayed.

Sixth Experiment: Measurement of Attrition Attributed to Grid Jets

Purpose

While attrition occurs in all parts of a fluidized-bed system, there appears to be appreciable attrition near the grid (distributor plate). We have investigated attrition in the bubbling-bed region above the grid in detail. The purpose of this experiment was to investigate and describe attrition near the grid.

Mechanism

At the grid gas issues forth from the grid orifices into the bed of particles. Along most of the jet length, as shown by films of jets in a bed, particles are swept into the jet.[A10,A12]

Once entrained in the jet, particles accelerate and smash into the roof of the jet, where they shatter into fragments.

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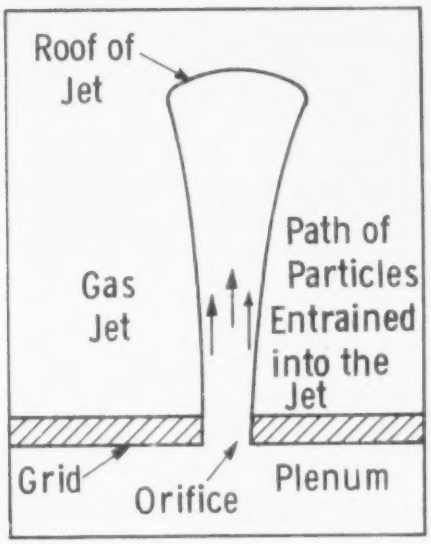

Characteristics of the system comprising this model are (Figure A17):

- Particles are entrained into the jet over most of its length at a flux F(Z) where Z is height measured aboveve the grid. Yang[A13] has measured the rate of particle entrainment into a jet for two lengths of jet exposure. His apparatus allows masking the top of a jet by directing it into a variable-height draft tube. Yang's results show that the rate of solids entrainment into a jet (mass/unit time) increases with the length of jet exposed above the orifice.
- Particles accelerate within the jet. The rate of acceleration vanes with radial position in the jet (Figure A16). The jet velocity decreases with Z because of the jet expansion (Figure A17). The velocity field within the jet is not the same as for a jet in a nozzle or a free jet in air. The entrained particles extract momentum from the gas, and the particles are entrained at some unknown rate.

- Particles strike the roof of the jet and shatter. The distribution of fragment sizes depends upon particle strength σ, particle velocity U_p, and particle diameter d_p. Fragment size distributions B (x, y) (Figure A18) have been studied for slow crushing or static crushing but have not been found reported for high-velocity impact.
- Particles circulate from the upper part of the jet to the base of the jet. Merry has shown that the particles may recirculate from the upper jet to the jet base and be reground in the jet (Figure A2).[A11]

Analysis

The foregoing description outlines an exceedingly complex momentary balance and circulation pattern. The system does not appear amenable to rigorous model analysis but seems best suited to dimensional analysis and experimental measurement of coefficients. The quantities involved in jet attrition are

Symbol	Description	Dimensions
R	attrition rate per jet	g/s
U_o	jet velocity at orifice	cm/s
ρ_s	particle density	g/cm^3
ρ_o	gas density at orifice	g/cm^3
d_p	particle diameter	cm
d_o	orifice diameter	cm
g	gravity acceleration	cm/s^2
g_c	Newton's law conversion factor	$g\ cm/m/dyne.s^2$
σ_s	particle strength	$dyne/cm^2$
Δs	increase in specific surface	cm^2/g

This list of variables, if each were tested, would present a formidable experimental program. "There exists a method between formal mathematical development and a completely empirical study. It is based on the fact that, if a theoretical equation does exist among the variables

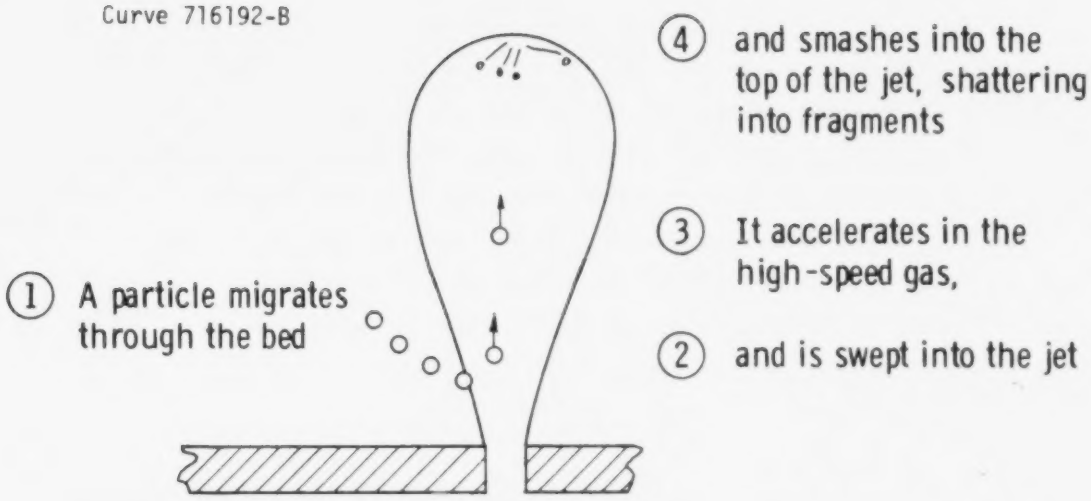
Curve 716192-B
4 and smashes into the top of the jet, shattering into fragments
3 It accelerates in the high-speed gas,
2 and is swept into the jet
1 A particle migrates through the bed

Figure A16. Movement of Particles through a Jet

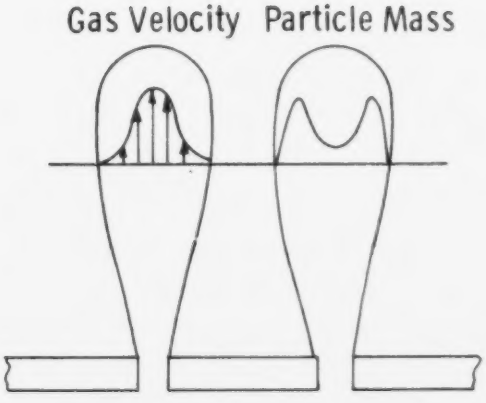

Figure A17. Conjectured Distributions of Gas Velocity and Particle Mass in a Fluidized-Bed Jet

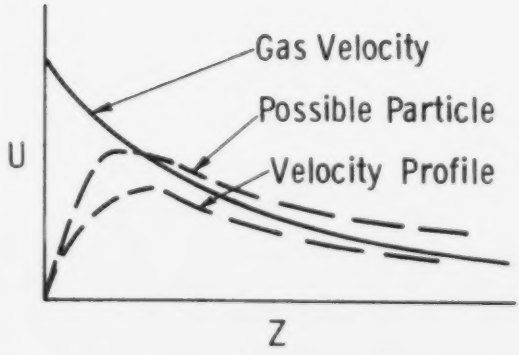

Figure A18. Variation of Particle Velocity and Jet Average Gas Velocity with Height above the Grid Z.

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Figure A19. Fragmentation Size Distribution B(x,y). Probably is affected by particle velocity before impact.

affecting a physical process, that equation must be dimensionally homogeneous. Because of this requirement it is possible to group many factors into a smaller number of dimensionless groups of variables."[A14]

The independent groups that can be formed from variables in the preceding list include

Dimensionless Group Name	Definition	Interpretation
N_{At} Attrition number	$\frac{R}{\rho_g U_o d_o^2}$	$\frac{\text{Rate of fines formation}}{\text{Rate of air mass delivered}}$
N_{Bo} Bond number	$\frac{d_o^2(g/g_c)}{(\sigma_s/\rho_s)}$	$\frac{\text{Gravitational force}}{\text{Attrition resistance}}$
N_{Fr} Froude number	$\frac{U_o^2}{gd_o}$	$\frac{\text{Inertial force}}{\text{Gravitational force}}$
N_D Diameter ratio	$\frac{d_p}{d_o}$	$\frac{\text{Particle diameter}}{\text{Orifice diameter}}$
N_ρ Density ratio	$\frac{\rho_g}{\rho_s}$	$\frac{\text{Gas density}}{\text{Solid density}}$

Our approach to describing jet attrition* was to measure the average rate of attrition in the grid region and relate it to dimensionless groups serving as independent variables. The actual attrition measurements were preceeded by a series of experiments for measuring sorbent hardness or attrition tendency (third and fourth experiments) in which

R = g of fines formed/s/jet

ρ_o = gas density at orifice, ρ_s = solids density, g/cm^3

d_o = orifice diameter, d_p = particle diameter, cm

U_o = gas velocity at the orifice, cm/s

g = gravity acceleration, cm/s^2

g_c = Newton's law conversion factor g . cm/dyne s^2

A0, A1, A2, A3, A4 = regression coefficients

σ_s = solid strength, dyne/cm^2

Apparatus

The apparatus we used in these tests was a a 7-cm-id vertical plastic tube filled with a single-hole grid. The grid was interchangeable for varying the orifice diameter. Figures A7 and A21 show the apparatus.

Procedure

In each test we filled the tube to depth of about 10 cm with a bed of sieved solids, set the gas flow, and let the bed jet for 5.0 minutes. During the test we recorded plenum pressure, rotameter float, and pressure readings; after the test we sieved the bed solids. Orifice gas density and temperature were calculated from a compressible-flow function table for isentropic gas expansion.

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*Some researchers[A15] question the existence of grid jets. We can as well consider this effect to be attrition caused by the high-velocity gas streaming from the grid orifices.

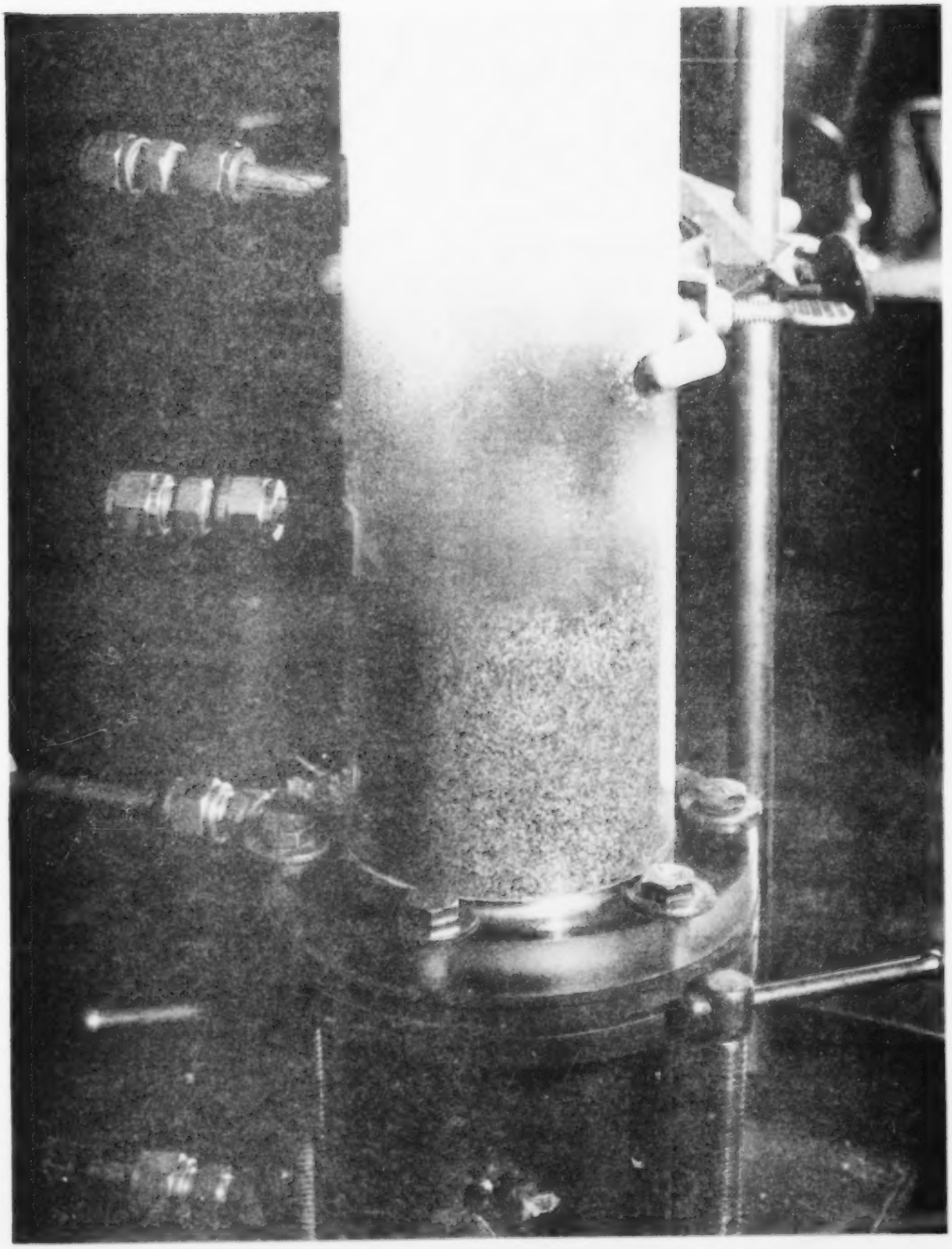

Figure A20. Close-up Photo of 7-cm-id Attrition Cell

Table A5

VALUES OF INDEPENDENT VARIABLES AND RESPONSES IN THE GRID JET ATTRITION TESTS

Test	Date 1978	Stone[a]	Gas	Orifice, cm	d_p cm	σ/ρ_s dyne·cm/g	ΔP psi	P_i psia	P_o/P_i	ρ_o/ρ_i	T_o/T_i	N_{BO}[b]	U_o[c]	N_{Fr}[d]	N_d d_p/d_o	ρ_o/ρ_p	Increase in Sp. Surf $\Delta s, cm^{-1}$	Increase in Fines Frac. ΔF	Increase in Mean Diam $\Delta d, \mu m$
J-1	5/2	Tuff	CO_2	0.157	0.0595 [e]	100	10	24.7	0.595	0.670	0.888	0.242	18452	2.21	0.379	0.0144	71.9	0.0755	135
J-2	5/2	Tuff	CO_2	0.157	0.1190 [f]	100	5	19.7	0.746	0.798	0.934	0.242	14440	1.36	0.758	0.0137	32.1	0.0322	159
J-3	5/2	Marble	CO_2	0.112	0.1190	457	10	24.7	0.595	0.670	0.888	0.027	18179	3.01	1.06	0.0101	1.8	0.0054	34
J-4	5/3	Tuff	Air	0.112	0.1190	100	10	24.7	0.595	0.690	0.862	0.123	23716	5.12	1.06	0.0098	31.0	0.046	155
J-5	4/28	Tuff	Air	0.157	0.0595	100	10	24.7	0.595	0.690	0.862	0.242	24322	3.84	0.379	0.0098	139.9	0.1223	310
J-6	5/3	Tuff	Air	0.157	0.0595	100	5	19.7	0.746	0.811	0.919	0.242	23656	3.64	0.379	0.0092	21.9	0.0334	54
J-7	5/4	Marble	CO_2	0.157	0.0595	457	5	19.7	0.746	0.798	0.934	0.053	14440	1.36	0.379	0.0096	17.8	0.054	77
J-8	5/3	Marble	Air	0.112	0.1190	457	4	18.7	0.786	0.841	0.933	0.027	19178	2.39	1.06	0.0063	6.8	0.0134	422
J-9	5/4	Marble	CO_2	0.112	0.0595	457	10	24.7	0.595	0.670	0.888	0.027	18179	3.01	0.531	0.0101	9.4	0.0439	43
J-10	5/4	Tuff	CO_2	0.157	0.1190	100	5	19.7	0.746	0.798	0.934	0.242	14440	1.90	0.758	0.0137	71.0	0.0584	269
J-11	5/5	Marble	Air	0.112	0.1190	457	10	24.7	0.595	0.690	0.862	0.027	23716	5.12	1.06	0.0069	6.8	0.0336	123
J-12	5/1	Marble	Air	0.112	0.0595	457	4	18.7	0.786	0.841	0.933	0.027	18897	3.25	0.531	0.0063	0.7	0.004	3
					0.1190	457	4	18.7	0.786	0.831	0.946	0.027	12956	1.53	1.06	0.0095	8.6	0.0329	130

a Stone Densities: Tuff 1.53 g/cm^3; Marble 2.18 g/cm^3

b $N_{BO} = (g/g_c)\, d_o^2\, /(\sigma_s/\rho_s)$

c $U_o = Q_o/A_o = Q^* (To/\rho_o) \sqrt{\rho^* P_R M^*/T_R T^* M_R} \div (\pi/4)\, d_o^2$

$= Q \quad = Q^* (To/14.7) \sqrt{14.7\, P_R\, 29/293 \cdot 293\, M_R} \div (\pi/4)\, d_o^2 = 0.006\, \frac{Q^* To}{d_R^2} \sqrt{\frac{P_R}{M_R}}$

M = Molecular Weight, * denotes reference conditions, o denotes conditions at orifice, I denotes conditions in plenum, R denotes conditions in rotameter

d U_o^2/gd_o

e 24 - 32 Mesh

f 12 - 16 Mesh

Results

Experimental results are listed in Table A5. Table A6 lists the associated regression expressions of the form

$$\text{Attrition} = A_0 + A_1 N_0 + A_2 N_{Fr} + A_3 N_d + A_4 N_\rho$$

and their error estimates, S_e. ($S_e \div$ halfrange) is the standard error estimate of the residual error. It is calculated as the normalized standard deviation of the differences between observed and predicted responses. S_e is an estimate of the standard deviation of the response at any setting of the independent variable. The coefficient of determination, R^2, is one measure of the quality of the model. It is the fraction of variation in the response which is accounted for by the model. The positive square root of R^2 is the correlation between the observed and predicted responses.

The normalized coefficients on different terms (Table A6) are comparable. For example the expression estimating $\Delta s x d_p^\circ$ has coefficients of 2.3, 0.3, 0.4, and 0.1 on the dimensionless variables. We can infer that the Bond number is predominant in estimating $\Delta s x d_p^\circ$.

Discussion

Inspection of the eight models investigated (Table A6) shows that the best estimates of grid jet attrition rate are described by the responses (dependent variables) involving specific surface. Note that in most models the Bond number $(g/gc)\, d_o^2/(\sigma_s/\rho_s)$ is prominent. The best fit (highest coefficient of determination, lowest relative standard error) in Table A6 is given by the last expression for $10^6\, \Delta s d^2/U_o t$). This expression, however, includes time as a linear variable ($\Delta s \alpha t$, and prior experience suggests that Δs is a power function of t, $\Delta s \alpha t^m$, $0 < m < 1$. For further discussion we consider the prior expression that gives a good fit and does not assume a constant attrition rate

$$(\Delta s \times d)^* = -0.279 + 0.54\, N_{Bo}^* + 0.069\, N_{Fr}^* + 0.109\, N_d^* + 0.143\, N_p^*$$

Table A6

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REGRESSION ANALYSIS RESULTS FOR GRID JET ATTRITION TESTING

Response	Regression Model (1)	$S_e \div$ (Range/2)	R^2 Coeff. of Determination
Increase in Specific Surface	$\Delta S = 37.3 + 27.3\, N_{Bo}^{\bullet} + 12.1\, N_{Fr}^{\bullet} - 9.1\, N_d^{\bullet} + 3.3\, N_\rho^{\bullet}$	0.483	0.58
Increase in Fines Fraction	$\Delta f = 0.051 + 0.002\, N_{Bo}^{\bullet} + 0.019\, N_{Fr}^{\bullet} - 0.012\, N_d^{\bullet} + 0.024\, N_\rho^{\bullet}$	0.486	0.42
Decrease in Mean Diameter	$\Delta d = 140.8 + 127.8\, N_{Bo}^{\bullet} - 95.1\, N_{Fr}^{\bullet} + 92.5\, N_d^{\bullet} - 142.8\, N_\rho^{\bullet}$	0.554	0.46
Attrition Number I	$N_{At} = 0.007 - 0.001\, N_{Bo}^{\bullet} + 0.004\, N_{Fr}^{\bullet} - 0.002\, N_d^{\bullet} + 0.003\, N_\rho^{\bullet}$ $\ell n\, N_{At} = -5.318 + 0.082\, N_{Bo} + 0.338\, N_{Fr} - 0.245\, N_d + 0.309\, N_\rho$ (2)	0.600 4.20	0.37 0.21
Sp. Surf. Incr. × Orifice Diam.	$(\Delta S x d_o)^{\bullet}$ (3) $= -0.489 + 0.4\, N_{Bo}^{\bullet} + 0.90\, N_{Fr}^{\bullet} - 0.113\, N_d^{\bullet} + 0.012\, N_\rho$	0.463	0.59
Sp. Surf. Incr. × Particle Diam.	$(\Delta S x d_p)^{\bullet}$ (3) $= -0.279 + 0.54\, N_{Bo}^{\bullet} + 0.069\, N_{Fr}^{\bullet} + 0.109\, N_d^{\bullet} + 0.143\, N_\rho^{\bullet}$	0.51	0.63
Attrition Number II	$10^6 \dfrac{\Delta S\, do^2}{Uo\, t}^{\bullet}$ (3) $= -0.489 + 0.18\, N_{Bo}^{\bullet} - 0.166\, N_{Fr}^{\bullet} + 0.05\, N_d^{\bullet} + 0.559\, N_\rho^{\bullet}$	0.43	0.70

(1) $N^{\bullet} = (N - \text{Midrange Value of Response}) \div \text{Halfrange of Response}$ $\quad N_{Bo}^{\bullet} = (N_{Bo} - 0.1345) \div 0.0175$ $\quad N_d^{\bullet} = (N_d - 0.72) \div 0.34$ $\quad N_{Fr}^{\bullet} = (N_{Fr} - 3.24) \div 1.88$ $\quad N_\rho^{\bullet} = (N_\rho - 0.01035) \div 0.00405$

(2) $N' = (\ell n\, N - \text{Midrange Value of } \ell n \text{ [response]} \div \text{Halfrange of } \ell n \text{ [response]}$

(3) $(\Delta S x d_o)^{\bullet} = \dfrac{\Delta S x d_o - 11.019}{10.941}$; $(\Delta S x d_p)^{\bullet} = \dfrac{\Delta S x d_p - 4.246}{4.204}$ $\quad \dfrac{\frac{6}{10} \Delta S d_o^2}{U_o t}^{\bullet} = \left[\dfrac{\frac{6}{10} \Delta S d_o^2}{U_o t} - 20.275 \right] \div 20.125$

The Bond number $d_o^2(g/gc) \div (\sigma_s/\rho_s)$ predominates and implies, first, that larger grid holes will increase attrition and, second, that harder material (larger σ_s) will attrite more slowly. The Froude number accounts for increased attrition with increasing gas velocity through the orifices. The density ratio infers that increasing gas density will increase attrition. This increase is expected because the denser gas provides a greater drag on particles and accelerates them faster in the jet. Similarly, the positive diameter ratio suggests that larger particles will attrite faster. This increase in speed, too, is expected where particles are accelerated to their terminal velocities in the jet: a larger particle exerts a greater kinetic-energy (α particle mass)/required-surface-energy (α particle surface) than does a smaller particle. For much larger particles that do not accelerate to the jet velocity before impact, however, the increase in attrition with particle size may not apply.

Knowing the increasing in specific surface, Δs, caused by jet action is of limited use in predicting fluidized-bed attrition. The increase in fines content, ΔF, is the needed practical variable. Regression analysis of the data in Table A5 gives us a relation between ΔF and Δs:

$$\Delta s = 1908\ \Delta F^{1.399};\ r = 0.92 \quad .$$

SCREENING TESTS: ATTRITION TENDENCY OF BROWNWOOD LIMESTONE

This work is described in the main text.

Conclusions

- Attrition can be severe in grid jets.
- Attrition in the vicinity of the grid occurs through entrainment of particles in a gas jet issuing from the grid, their acceleration in the jet, and their being thrown at high velocity against the roof of the jet.

- This is a complex mechanism, and the separate processes comprising the mechanism are unknown. The overall mechanism is not easily amenable to modeling and analysis.
- The overall mechanism is amenable to dimensional analysis in which seven independent variables can be combined into four independent dimensionless groups.
- Experimental attrtrition results correlate well with linear combination of four dimensionless groups (the Bond number, Froude number, diameter ratio, and density ratio).

Seventh Experiment: Testing for Attrition Tendency of Fluidized-Bed Gasification Sorbents

The full text of this experiment is in the main text.

Summary

Fluidized beds are well suited to gasification of coal. The bed solids, chemically-active limestone or dolomite, capture sulfur pollutants as soon as they are released from the coal. The continued agitation of particles in a bed, however, causes attrition to fines and a subsequent loss of solids.

Natural materials vary in their resistance to attrition. To select sorbents one must screen them by some laboratory procedure. The purpose of this study is to develop a reproducible procedure for measuring the attrition resistance of granular sorbents.

Coal gasifiers encounter temperatures of about 800 to 900°C. Sorbent added to an operating bed first experiences thermal shock, then calcination. Jets at the grid and bubbling above the grid tumble the sorbent particles. The sorbent screening process we have developed includes all of these processes to attrite particles by thermal, chemical, and mechanical means.

The test apparatus is a 9.5-cm-id cell with a three-hole grid. Test temperatures are maintained by a furnace surrounding the cell. Our test procedure was to determine the gas flow required to form 8-cm-high jets in a bed of a particular sorbent. Sorbent was added to an empty bed at 900°C and fluidized for one hour at 815°C at the predetermined gas flow rate. Solids were sieved for particle size distribution before and after the attrition treatment.

Replicate testings of Grove, Greer, Brownwood, and Pfizer sorbents showed good repeatability between replicate tests and decisive differences in attrition tendency among different sorbents.

The apparatus and procedure developed in this study are not presented as a universal method but rather as a prototype. This study demonstrates that sorbents can be ranked decisively with regard to attrition tendency.

Conclusions

- We have demonstrated an apparatus and a procedure for measuring the attrition tendency of granular sorbents.
- The procedure includes the attrition mechanisms present in the grid region, the bubbling bed region, splashing in the freeboard, thermal shock, and calcination.
- The procedure for sorbent screening tested in this study discriminates decisively between the attrition tendencies of different sorbents.
- We do not propose the apparatus and procedure described here as a standard. This method serves as a prototype and demonstrates that a standard screening method can be developed.

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